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SPECTRES D'ABSORPTION INFRAROUGES DES URÉES SUBSTITUÉES[1]

PAR JEAN L. BOIVIN ET PAUL A. BOIVIN

RÉSUMÉ

Les spectres d'absorption infrarouges de quelques urées substituées par des groupements alkyles ou aryles ont été déterminés entre 2 et 15 μ. Les urées du type $RNHCONHCH_3$ donnent à 7.05 μ une bande d'absorption constante qui semble caractériser le groupement $CH_3NH\ CONH-$. Suit une explication générale des spectres obtenus avec les différents dérivés de l'urée.

INTRODUCTION

Le spectre d'absorption infrarouge de l'urée est bien connu, mais difficile à expliquer. On obtient l'absorption caractéristique des groupements NH et CO, mais non pas aux longueurs d'onde normales des amides. Comme l'urée est une diamide qui possède toutes les propriétés des amides aliphatiques, on devait s'attendre à un comportement identique en spectrométrie infrarouge.

Afin d'expliquer le spectre de l'urée, on a déterminé les spectres infrarouges de quelques urées substituées sur l'azote en position 1 ou 3. Leur préparation a déjà été décrite dans une publication précédente (1).

La littérature fait mention de plusieurs travaux où le spectre infrarouge de l'urée est surtout étudié du point de vue de la mécanique quantique. Peu de travaux sur les spectres d'absorption infrarouges expliquent sa structure chimique.

Récemment, Pristera (2) a publié les spectres de la diméthyldiphénylurée et de la diéthyldiphénylurée et a attribué les bandes obtenues à 6.00 μ et 6.70 μ aux groupements carbonyles et carbamides. La dernière bande d'absorption semble avoir été confondue avec celle du noyau aromatique qui apparaît à 6.25 μ et 6.70 μ.

Mesures spectrophotométriques

On a utilisé un spectrophotomètre Perkin–Elmer, modèle 21 à doubles faisceaux, pour déterminer les spectres d'absorption infrarouges des urées. Les courbes de transmission étaient enregistrées automatiquement sur cet appareil.

Une émulsion des produits dans l'huile minérale servit à la détermination des spectres. Pour obtenir un spectre convenable, l'épaisseur de l'émulsion

[1] *Manuscrit reçu le 18 janvier 1954.*
Contribution du Département de Chimie, Université d'Ottawa et du Conseil des Recherches pour la Défense, C.A.R.D.E., Valcartier, Québec.

fut variée de façon à ce que les bandes d'absorption aient une bonne intensité. On ne donne que deux courbes de transmission (fig. 1), celles des cyclo-

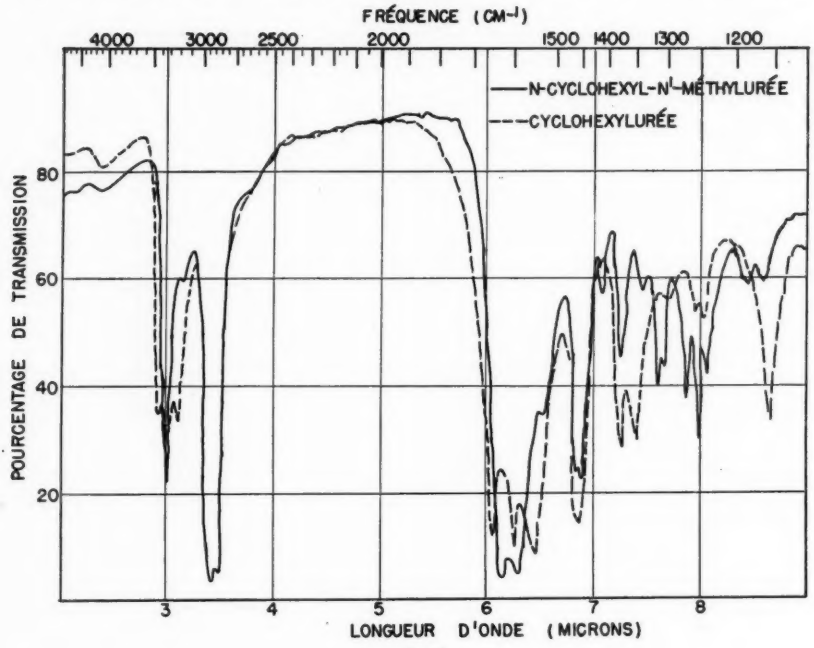

FIG. 1

hexylurées. Pour les spectres des autres produits, les longueurs d'onde des bandes de bonne intensité seulement sont rapportées dans les tableaux I and II.

Urées substituées en position 1

Ces urées (tableau I et fig. 1) donnent des bandes d'absorption dans les régions de 3 μ et de 6 μ qui caractérisent les groupements NH, NH_2 et C=O. Dans la région de 3 μ, la plupart des composés que nous avons étudiés possèdent trois bandes d'absorption; chacune correspond à un mode de vibration entre les atomes d'hydrogène et d'azote. Deux bandes d'absorption et parfois trois sont bien distinctes, mais la troisième est souvent un point d'inflexion. On pourrait attribuer aux vibrations N–H les bandes d'absorption obtenues entre 2.90 μ et 2.96 μ; et aux vibrations NH_2, celles produites entre 2.98 μ et 3.15 μ.

Les possibilités d'avoir des vibrations OH sont exclues, car ces urées ne se tautomérisent pas facilement en milieu neutre:

TABLEAU I
Urées substituées ($RNHCONH_2$)

Substituants	Position des bandes en microns																				
Méthyle	2.92	3.01		6.08	6.38				7.05				8.58	9.05	11.05	12.80	13.90				
Éthyle	2.92	2.98	3.10		6.05	6.23	6.40		7.45				8.64	9.05	9.27	11.30	12.70	13.90			
n-Propyle	2.95	3.10		6.04	6.22	6.43			7.40	7.72	8.00		8.62	9.00	11.18	11.60	12.80	13.33			
n-Butyle	2.95	3.04	3.17		6.02	6.12	6.54														
n-Amyle	2.95	3.10		6.03	6.12	6.23	6.51	6.75	7.45	7.67			8.68	8.90	12.80	13.65					
n-Hexyle	2.94	3.10		6.03	6.12	6.23	6.53	6.75	7.37	7.55	7.78		8.68	8.90	13.85	13.70					
Cyclohexyle	2.92	2.98	3.10		6.05	6.25	6.45		7.40	7.70	7.95	8.02	8.64	9.70	11.20	13.45	12.82	13.90			
Phényle	2.90	3.00		6.02	6.17	6.25	6.44	6.67	7.36	7.95			8.95	9.28	9.65	11.05	11.65	12.94	13.32	14.40	
Benzyle	2.92	2.98		6.07	6.23	6.38			7.52	7.63	8.27		8.74	9.04	9.25	9.75	10.98	12.10	13.25	13.35	14.40
Anilino	2.92	2.97	3.12		6.02	6.23	6.68		7.00	7.12	7.65	7.88	8.62	9.02	9.28	9.75	11.27	12.90	13.20	13.30	14.50
p-Tolyle	2.92	3.02		6.05	6.27	6.45	6.60		7.12	7.35	7.67	7.95	9.02	12.14	12.32	12.84	14.15				
p-Chlorophényle	2.92	3.00		6.04	6.20	6.28	6.45	6.70	7.62	7.72	7.84	8.00	9.15	9.85	11.50	12.20	12.94	13.70	14.65		

TABLEAU II
1-Méthylurées substituées en position 3 ($RNHCONHCH_3$)

Substituants	Position des bandes en microns																						
Méthyle	2.98	3.14*		6.15					7.50	7.80						8.52	9.60	10.74	12.90				
Éthyle	2.98		6.12	6.32					7.05	7.90						8.56	9.20	9.50	11.10	12.90			
n-Propyle	3.00	3.15*		6.12					7.05	7.90						8.60	9.35	11.05	11.20	12.90	13.15		
n-Amyle	2.98		6.16						7.05	8.60													
n-Hexyle	2.98		6.02	6.08	6.15	6.25	6.58		7.05	7.70	7.95	8.13				8.60	12.95	13.75					
Cyclohexyle	2.99		6.02	6.08	6.15	6.30	6.52		7.05	7.45	7.60	7.68	7.98	8.07	8.44	8.62	9.23	11.27	11.82	12.94			
Phényle	2.96	3.00*	6.08	6.15	6.25	6.30	6.47	6.65	6.92	7.05	7.60	7.95				8.55	9.25	11.05	11.70	11.84	13.2	13.65	14.35
Benzyle	2.98		6.15	6.32	6.67	7.02				7.05	7.34	7.78	7.90			8.60	9.27	9.52	9.75	13.65	14.32		
p-Tolyle	2.98		6.05	6.23	6.40	6.60				7.05	7.12	7.62	7.68	7.85	8.08	8.56	9.00	11.90	12.33	12.92	13.17	14.15	
p-Chlorophényle	3.00		6.10	6.22	6.35	6.57	6.72			7.05	7.15	7.70	7.79	8.05		8.56	9.17	9.88	12.02	12.25	13.20	13.50	13.90	14.60

**Point d'inflexion*

Dans la région de 6 μ, qui caractérise les composés à doubles liaisons, une seule bande d'absorption apparaît dans l'analyse de ces urées substituées, entre 6.02 μ et 6.12 μ. On peut donc les apparenter au groupement carbonyle de l'urée. D'ailleurs les amides primaires absorbent habituellement entre 5.90 μ et 6.25 μ.

Une autre bande d'absorption de bonne intensité apparaît aux environs de 6.20 μ. Lorsque R est un radical aliphatique, cette bande semble due à la déformation de NH_2 qui apparaît entre 6.08 μ et 6.25 μ. Mais lorsque R est un résidu aromatique, le noyau benzénique absorbe entre 6.20 μ et 6.25 μ et donne une bande d'intensité variable, mais toujours présente à ces longueurs d'onde.

Dans la région entre 8.00 μ et 9.00 μ, il y a absorption caractéristique pour tous les composés substitués par un groupement aliphatique. On peut observer un déplacement bathochromique lorsque l'on passe d'un substituant méthyle à éthyle, propyle, butyle, amyle et hexyle (tableau I).

Il y a plusieurs bandes d'absorption entre 9 μ et 15 μ. Cette région du spectre infrarouge caractérise toute la molécule et ne peut servir qu'à l'identification du composé lui-même.

1-Méthylurées substituées en position 3

Les 1-méthylurées substituées en position 3 donnent des spectres d'absorption infrarouges différents des urées monosubstituées (tableau II et fig. 1).

Dans la région de 3 μ, on obtient des bandes intenses qui indiquent la présence de vibrations NH. Avec les urées, $RNHCONH_2$, on observe trois bandes d'absorption correspondant aux trois modes de vibration entre les atomes d'hydrogène et d'azote. Les urées du type $RNHCONHCH_3$, ayant deux groupements NH ou deux modes de vibration, devraient donner deux bandes d'absorption; mais il n'y a qu'une forte bande d'absorption à 2.98 μ. Toutefois, on obtient un point d'inflexion à une plus grande longueur d'onde (3.10 μ–3.20 μ). La possibilité de tautomérisation de ces urées est encore minime ou inexistante.

Dans la région de 6 μ, i.e. la longueur d'onde normale où les amides ordinaires donnent des bandes d'absorption, les composés du type $RNHCONHCH_3$ donnent tous une absorption intense. Cette bande est due au groupement C=O de ces urées. Il semble y avoir un déplacement de cette bande à mesure que le radical passe de éthyle à hexyle. De 6.20 μ à 6.25 μ et de 6.65 μ à 6.70 μ, on retrouve les absorptions dues aux groupements phényles des urées substituées.

A 7.05 μ, on obtient une bande de bonne intensité qui est présente dans le spectre de toutes les urées du type $RNHCONHCH_3$. Cette bande semble caractériser le groupement $CH_3NHCONH$–. En considérant le tableau I, on constate que la méthylurée donne également une absorption à 7.05 μ.

Etant donné le nombre de composés étudiés et la variété de leurs substituants, il est possible d'identifier le groupement $CH_3NHCONH-$ à l'aide de cette bande.

Entre 8.50 μ et 8.60 μ, on observe également l'effet de la chaîne hydrocarbonée. Ainsi, il y a encore un déplacement bathochromique en passant du groupement méthyle à hexyle.

Si l'on compare les spectres de ces urées, $RNHCONH_2$ et $RNHCONHCH_3$, à celui de l'urée ordinaire, on observe que les bandes à 3.00 μ et 6.00 μ ne sont pas à la même longueur d'onde, bien qu'elles soient présentes dans ces régions du spectre. Ces mesures ont permis d'identifier le groupement méthylcarbamido ($CH_3NHCONH-$) et de conclure que les urées substituées se comportent en spectrographie infrarouge comme des amides ordinaires.

SUMMARY

The infrared spectra of N-substituted ureas and N′-methyl-N′-substituted ureas have been determined in mineral oil emulsion from 2 μ to 15 μ. It was found that all the ureas of formula $RNHCONHCH_3$ gave an absorption band at 7.05 μ which seems to be characteristic of the methylcarbamido group ($CH_3NHCONH-$).

REMERCIEMENTS

Les auteurs désirent remercier monsieur Marcel Bédard, C.A.R.D.E., qui détermina les spectres d'absorption infrarouges et le Conseil des Recherches pour la Défense qui permit la publication de ce travail.

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A STUDY OF THE SULPHATE ESTER OF UNSTABILIZED CELLULOSE ACETATE[1]

By Karl Keirstead and John Myers

ABSTRACT

Evidence for the existence of the ester form of the sulphate in unstabilized cellulose acetate has been examined by ion exchange studies on precipitated and fibrous cellulose acetate. The equilibrium reached during ion exchange is affected by the pH and by the concentration of the salt solution used. The thermal stability of the ester is shown to vary inversely with the sulphate content. A study has been made of the accuracy of the various analyses involved.

INTRODUCTION

Cellulose acetate and cellulose nitrate are normally prepared by treatment of cellulose with the appropriate acid in the presence of sulphuric acid at the appropriate temperature. At one stage in the preparation both esters contain a small amount of sulphate. The amount depends on the composition of the esterifying medium and other factors but usually it is less than 1%. Purification or stabilization, as it is usually called, may be accomplished by partial hydrolysis of the ester in the appropriate medium. It has been established by Malm *et al.* (10) that the sulphate in unstabilized cellulose acetate is in the form of a sulphate ester, RSO_4H, but its form in unstabilized cellulose nitrate has been the subject of discussion for many years. Some direct evidence for the existence of a sulphate ester in cellulose nitrate was presented by Reeve and Giddens (12) in connection with a study of the mechanism of stabilization by ammonia. Freshly prepared samples of cellulose nitrate, rinsed free of superficial acids, were treated with 1% aqueous ammonia at room temperature for 15 min., then thoroughly rinsed and dried for sulphate and ammonia determinations. The results showed that the ammonia–sulphate relation for the unboiled samples was close to unity, suggesting that the sulphate was present in the hemiester form, RSO_4H. Previously Kullgren (9) had estimated the hemiester content of nitrocellulose by the use of an ion-exchange method. The acid liberated from the exchange as indicated below

$$RSO_4H + NaCl \longrightarrow RSO_4Na + HCl \qquad [1]$$

was taken to be a measure of the hemiester content. For one particular sample this value was 25% of the sulphate content. Kullgren (9) concluded that a large part of the sulphate (75%) must be present as the neutral sulphate, R_2SO_4.

The experiments described in this report were undertaken to establish the relative merits of various ion exchange methods for the estimation of the sulphate ester of cellulose acetate. The possibility of applying these methods to the estimation of the acid ester content of cellulose nitrate will be reported in a later communication. While many investigations have been made on ion

[1] *Manuscript received February 2, 1954.*
Contribution from Canadian Armament Research and Development Establishment, Valcartier, Quebec.

exchange with naturally-occurring minerals and more recently with synthetic organic resins, the only detailed study of ion exchange with cellulose acetate sulphate appears to have been carried out by Araki and Tadenuma (1) who used a "sulphoacetate gel". Because of the present unavailability of the original report it is impossible to make further reference to this study. It should be noted, however, that the present work has been carried out with cellulose acetate sulphate in the precipitated and fiber forms. The term "cellulose sulphoacetate" has been used generally to refer to products with a high sulphate content, but as pointed out by Malm it should be applied only to an ester of cellulose with sulphoacetic acid. Following the terminology used for mixed organic esters of cellulose, the mixed ester of acetic and sulphuric acids will be termed cellulose acetate sulphate.

Cellulose acetate sulphate consists of a high-polymer structure to which sulphate groups with ionizable hydrogen are attached. The whole compound may be regarded as an insoluble acid and its behavior may be studied by determining the change in pH when a suspension is titrated with alkali under various conditions (7, 15). When sodium hydroxide is added to a suspension of cellulose acetate sulphate in the absence of neutral salt the pH changes

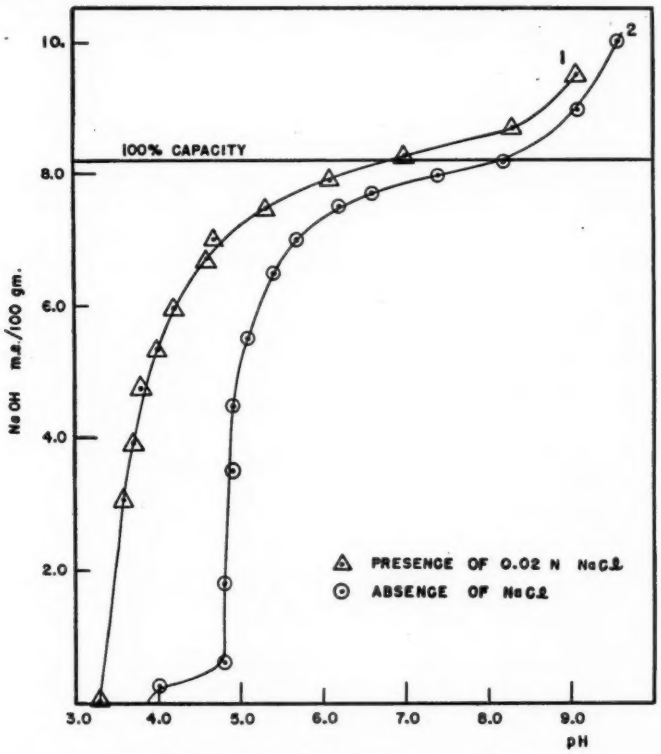

FIG. 1. Titration of cellulose acetate sulphate.

only slowly until the amount added is equivalent to most of the acidic hydrogen on the exchanger, which is known as the full capacity. When 0.2 *N* sodium chloride is added to the system, it becomes acid and the full capacity is realized at pH 7 as shown in Fig. 1. In all the experimental work great care must be taken to avoid or correct for hydrolysis of the sulphate and acetate groups in water. Prior to all experiments hydrolysis was minimized by thorough washing with distilled water, and the effect during an experiment was limited by keeping the duration to a minimum or by estimating the amount of acid formed.

There are a number of methods of studying the ion exchange process quantitatively. If an ion exchange takes place according to the equation

$$RSO_4H + M^+ \longrightarrow RSO_4M + H^+ \qquad [2]$$

the hydrogen ion concentration in the solution after exchange and the metal content of the ester expressed in milliequivalents should each be equal to the sulphate content of the fiber. Malm (10) showed that the sulphate content of unstabilized cellulose acetate sulphate determined by repeated treatment with 1% sodium chloride solution followed by titration of the hydrogen ion liberated in the combined filtrates was 1.01% compared with 1.05% determined by sulphate estimation.

The present paper considers the relations among the sulphate contents as determined by the three possible methods.

EXPERIMENTAL RESULTS

Ion Exchange Experiments

Table I shows the amount of sulphate found in various samples of cellulose acetate by the determination of sulphate gravimetrically as the barium salt, and by ion exchange with sodium or calcium chloride solution and subsequent titration with standard sodium hydroxide.

TABLE I
COMPARISON OF TITRATION AND GRAVIMETRIC METHODS OF DETERMINING SULPHATE ESTER

Batch No.	Type	Cation exchanged	Sulphate, m.e./100 gm.		Per cent difference
			Gravimetric	Ion exchange titration	
28-6	Fiber	Ca	29.3	25.7	−12
33	"	"	23.7	19.5	−18
29-1	"	"	13.6	10.7	−21
29-2	"	"	9.3	6.2	−34
20	Pptd.	"	9.1	8.8	− 3
29-3	Fiber	"	6.5	3.8	−41
32	Pptd.	"	0.20	0.19	− 5
19-13	Fiber	Na	13.6	12.4	− 9
19-1	"	"	13.6	12.4	− 9
17	Pptd.	"	8.0	7.1	−11
23	"	"	6.5	6.1	− 6
27-1	Fiber	"	2.9	2.2	−14
27-2	"	"	2.5	2.3	− 8
27-7	"	"	2.5	2.3	− 8

The normality of the salt solution was 0.2 and the pH was 5.7. In all experiments, the sulphate content determined by ion exchange was less than that found gravimetrically, and it will be shown below that the difference is well outside the expected experimental error. It can be accounted for either by incomplete ion exchange reaction or by adsorption of hydrogen ions on the sample. Table II shows that the second alternative is more likely because the sulphate determined by estimation of the exchanged calcium agreed more closely with the sulphate determined gravimetrically than with that determined by titration of hydrogen ion.

TABLE II
COMPARISON OF CALCIUM AND GRAVIMETRIC METHODS OF DETERMINING SULPHATE ESTER

Batch No.	Type	Sulphate, m.e./100 gm.		Per cent difference
		Gravimetric	Calcium	
28-6	Fiber	29.3	28.6	−2.4
33	"	23.8	24.5	+3.0
45	"	20.5	20.8	+1.0
36	"	17.2	18.2	+6.0
43	"	16.6	16.9	+2.0
40	"	14.9	15.2	+2.0
29-1	"	13.6	13.8	+1.0
30	Pptd.	26.5	26.7	+1.0

The results obtained by the two methods agreed within the limits of experimental error, suggesting that the discrepancies between the gravimetric and titration methods were caused by adsorption of hydrogen ions.

In some of the experiments in which 0.2 *N* sodium chloride solution was used for the exchange, the sodium on the sample after exchange was determined by flame photometry. A few results are shown in Table III. Sample

TABLE III
COMPARISON OF SODIUM AND GRAVIMETRIC METHODS OF DETERMINING SULPHATE ESTER

Batch No.	Sulphate, m.e./100 gm.		Per cent difference
	Gravimetric	Sodium	
17-4-a	8.0	4.6	−42.5
17-8-a	7.7	3.5	−55.0
17-8-6	7.7	3.0	−61.0
39-7	11.3	11.3	0

39-7 was subjected to three rapid washes with distilled water after exchange while no particular care was taken in washing the other three samples. The removal of sodium by washing was confirmed by the increase in ion exchange acidity after washing and the presence of sodium in the filtrate. In one experiment a sample regained 25% of the ion exchange capacity after continuous washing for five hours, followed by contact with water for three days, and in others 100% of the ion exchange capacity was recovered after washing for seven days.

It was found that the physical state of the sample had a considerable influence on the ion exchange process. A sample of batch 29-1 was boiled for five minutes in water and then for 10 min. in 50% alcohol (29-2) while another sample was boiled for five minutes in water followed by five minutes in absolute alcohol (29-3). The sulphate determined by the gravimetric, titration, and calcium methods is shown in Table IV.

TABLE IV
EFFECT OF SAMPLE TREATMENT ON ION EXCHANGE

Batch No.	Sulphate				
	Gravimetric, m.e./100 gm.	Titration		Calcium	
		m.e./100 gm.	Per cent difference	m.e./100 gm.	Per cent difference
29-1	13.6	10.7	−21.0	13.8	+ 1.4
29-2	9.3	6.2	−33.6	9.3	0
29-3	6.5	3.8	−41.5	7.8	+20.0

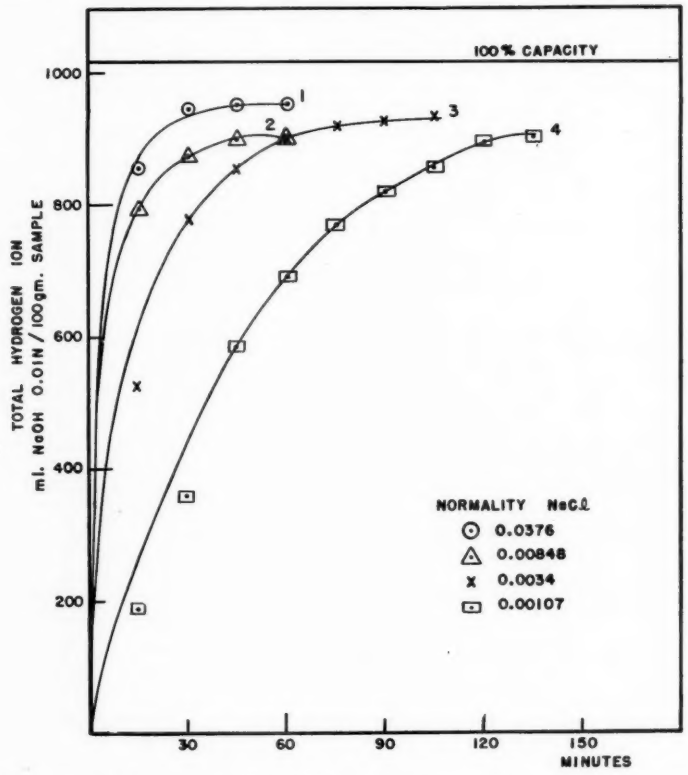

FIG. 2. Effect of salt concentration on Na^+–H^+ exchange, cellulose acetate sulphate (18-6).

The alcohol treatment modified the exchange process considerably and it can be seen that the errors with the titration method were large. In the third sample the sulphate determined by the calcium method was high, suggesting that the calcium ions may also be adsorbed.

The effect of the normality of the salt solution is demonstrated in Fig. 2, which shows some curves of acidity against time for exchange in sodium chloride solutions. With normalities greater than 0.01, exchange was quite rapid but below this normality the time for exchange increased rapidly.

The effect of pH on exchange in a 0.2 *N* sodium chloride solution is shown in Table V for two samples of ester.

TABLE V

EFFECT OF pH ON ION EXCHANGE

Batch No.	Type	Sulphate, m.e./100 gm., gravimetric	pH	Sulphate, m.e./100 gm., titration.	Per cent difference
19-9	Fiber	13.6	8.6	13.4	− 1
"	"	"	6.7	12.8	− 5
"	"	"	5.75	12.7	− 6
"	"	"	4.5	12.3	− 9
"	"	"	3.8	12.1	−10
21	Pptd.	10.1	10.5	9.3	− 8
"	"	"	8.8	6.1	−40
"	"	"	3.9	5.2	−49
"	"	"	1.9	2.8	−72

The sulphate determined by titration was very sensitive to pH, particularly for precipitated samples.

Heat Stability of Cellulose Acetate Sulphate

Commercial methods for the determination of the thermal stability of cellulose acetate depend either on the charring temperature or the liberation of acetic acid by hydrolysis of the moist sample (4). In the present investigation the stability of the mixed ester was determined by a heat test used previously for unstabilized nitrocellulose. The test has been adapted from the 110°C. test described by Reeve and Giddens (12). Dry air at 65 ± 0.5°C. was used to sweep decomposition products from the sample and an iodometric method used to detect the first traces of volatile acid. The time in minutes taken for a change in the color of the indicator is regarded as a measure of the stability of the sample. Some typical results are shown in Table VI, each value being the mean of several determinations.

The stability of samples of fiber was increased by the substitution of hydrogen by calcium but in one sample of precipitated material examined, ion exchange decreased the stability. The stability of the precipitated material was very much greater than that of the fiber material. Preliminary studies on unstabilized cellulose nitrate using the same test have indicated an increase in stability after ion exchange. In one experiment the stability time for the

TABLE VI
HEAT STABILITY OF CELLULOSE ACETATE SULPHATE

Batch No.	Type	Sulphate content, mgm. H_2SO_4/100 gm.	Stability (minutes)	
			Untreated	Ca treated
56	Fiber	193	13.2	
"	"	228	11.8	
"	"	313	9.2	
52	"	805	8.5	
18	"	944	4.3	
29	"	1340	2.5(2.3, 2.7)*	
40	"	1468	2.0	3.0
28	"	2870	1.7(1.3, 2.1)	3.2
32	Pptd.	195	70.0 (71.0, 71.5, 68.0)	56.8 (56.8, 56.6, 57.0)
51	"	1080	38.4	
44	"	1661	5.0	

**Figures in brackets are duplicate determinations.*

untreated sample was six minutes. After ion exchange with calcium, the stability time was increased to 41 min.

Determination of Dry Weight

The poor stability of cellulose acetate sulphate precludes the use of a heated oven for drying the samples. The decomposition effected by heating resulted in a detectable odor of acetic acid in samples dried at 65°C. It was found that decomposition could be reduced to a minimum by vacuum drying at room temperature. The moisture determined by this method agreed within 1% with that obtained by drying at 40°C., 60°C., and over phosphorus pentoxide at room temperature. The acetyl content of the vacuum-dried material agreed within 1% with the value found on the damp sample. Unlike the product dried in excess of nine hours over phosphorus pentoxide, the vacuum-dried samples showed no change in color. Where possible, experiments were done with a damp sample. Two methods were used to obtain the dry weight. In the first method the dry weight was found by determining the moisture content of a portion of the sample and in the second, the sample was dried after the experiment.

DISCUSSION

The results reported above showed that sulphate content determined by titration of the hydrogen ion liberated by ion exchange with sodium or calcium chloride was always less than that determined gravimetrically as barium sulphate. In most cases the results obtained by estimation of calcium on the sample after ion exchange agreed with the gravimetric results within the limits of the experimental error, but it was found that those obtained by the determination of sodium were usually low and special precautions were essential during the washing of the sample to prevent removal of sodium. It was also demonstrated that treatment of the sample by boiling in alcohol, and the pH of the exchange medium, greatly affected the results. The equilibrium between the sodium and hydrogen ions is apparently quite critical

and affected greatly by small changes in experimental technique. There was some evidence to suggest that adsorption of hydrogen ions by the sample was responsible for the low results obtained by the titration method and the results in Table IV show that, under certain conditions, calcium ions were adsorbed. Determination of calcium on the sample after ion exchange with calcium chloride solution gave the best results for the amount of sulphate present as RSO_4H.

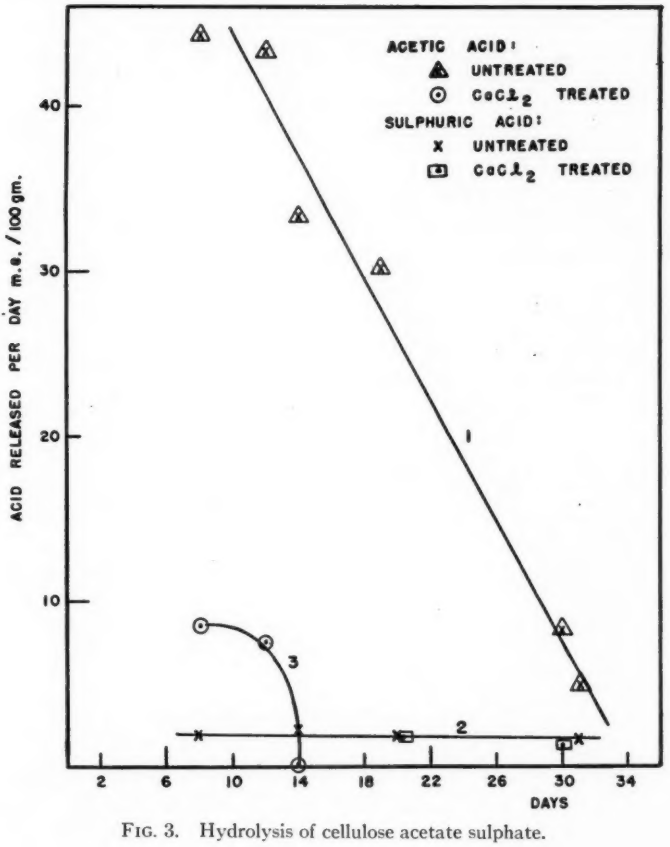

FIG. 3. Hydrolysis of cellulose acetate sulphate.

The greater stability of the calcium-treated fiber samples as determined by the stability test described was in agreement with the greater stability to hydrolysis of the treated material as shown below. Further work is required to determine the decreased stability of the precipitated sample after treatment with calcium chloride, and also to investigate the very large difference between the stability of the fiber and precipitated samples. The difference in physical form may be responsible for the latter effect.

Precision and Accuracy of the Methods

Hydrogen Ion

The amount of free acid in the sample was reduced to a minimum before an experiment by giving 2.5 gm. samples five-minute washes in 100 ml. of distilled water until the acidity was less than the equivalent of 0.80 ml. of 0.01 *N* sodium hydroxide. The rate of formation of acid by hydrolysis from a typical sample containing about 1.6% of sulphate is shown in Fig. 3 for a 30-day period. The amount of acetic acid released per day decreased rapidly while the amount of sulphuric acid decreased only slightly. Another sample was examined after ion exchange with 0.02 *N* calcium chloride. It can be seen that the amount of acetic acid formed was much less and reached zero after a few days, while the sulphate hydrolysis was not affected. The increased stability of the salt form of cellulose esters has been observed previously by Hoffpauir and Guthrie (8). All samples were normally stored in distilled water until required and then used within 4 to 14 days. It was shown that the amount of acid liberated by hydrolysis during an experiment could be regarded as negligible.

Sulphate

Known amounts of standard solution of sulphuric acid were added to samples of a batch of low sulphate content. The total sulphate was determined in triplicate and compared with the figure calculated from the known initial content and added amount. The results are shown in Table VII.

TABLE VII

PRECISION AND ACCURACY OF SULPHATE DETERMINATION IN CELLULOSE ACETATE

Initial sulphate found, mgm. of H_2SO_4	Sulphate added, mgm. of H_2SO_4	Total sulphate	
		Calc.	Found
5.03 ± .25	4.90	9.93	9.96 ∓ .20*
"	9.81	14.84	14.84 ∓ .43
"	14.71	19.74	19.65 ∓ .15
"	19.62	24.65	24.65 ∓ .15
"	24.53	29.55	29.59 ∓ .13

**The 95% confidence level.*

From the 95% confidence level calculated by the method of Dean and Dixon (2) from the triplicate determinations it can be seen that the average value was precise to better than 1% when the sulphate level was greater than 20 mgm. sulphuric acid, which is equivalent to 10.2 m.e./100 gm. It is concluded that the accuracy and precision of the method are better than 1% except for sulphate concentrations below 10 m.e./100 gm.

Calcium

Precision and accuracy were determined by adding known amounts of a standard calcium solution to samples of cellulose acetate sulphate. Determinations were made in triplicate and a correction made for the blank done on the original sample. The results are shown in Table VIII.

TABLE VIII
PRECISION AND ACCURACY OF THE CALCIUM DETERMINATION

Calcium added, mgm.	Calcium found, mgm.
10	9.91 ∓ 0.09
25	24.81 ∓ 0.10

The 95% confidence levels calculated by the method of Dean and Dixon (2) show that the precision was better than 1%, although both results were about 1% low.

EXPERIMENTAL METHODS

Materials

Cellulose

Two kinds of cellulose were used for acetylation:

(*a*) *Wood cellulose.*—B.C. rayon pulp having the following analysis: α-cellulose, 91.7%; ash, 0.07%; iron, 0.0002%. This cellulose was supplied by Canadian Industries Limited.

(*b*) *Cotton linters.*—High grade cotton linters were supplied by the Hercules Powder Company.

Acetone

The acetone, supplied by the Standard Chemical Company, was redistilled before use.

Cellulose Acetate Sulphate (Solvent Process, Batch No. 21)

Malm's method (10) was followed.

Cellulose (40 gm., 1 part) was added to acetic acid (96 gm., 2.4 parts) and stirred for one hour at 38°C. A mixture of acetic acid (160 gm., 4 parts) and sulphuric acid (0.352 gm.) was then added. Mixing was continued for 45 min. After cooling to 15°C. a mixture of acetic anhydride (108 gm., 2.7 parts) and sulphuric acid (2.45 gm.) was added. The temperature rose to 30°C. in an interval of two hours by which time the cellulose had dissolved. A drop of the dope when pressed between two microscope slides and examined with a magnifying glass showed only traces of fibers.

A mixture of acetic acid (80 gm., 2 parts) and water (80 gm., 2 parts) was added during a five minute period. After the aqueous acetic acid was added and thoroughly mixed, the dope was transferred to a hydrolysis bath at 35°C. After 24 hr., the dope was slowly poured into distilled water stirred at high speed in a Waring blendor.

The precipitated cellulose acetate sulphate had a moisture content of 92.7% after it had been washed with distilled water, sucked dry on a Buchner funnel, and pressed between filter paper. Analysis: apparent acetyl 32.2%; sulphate, 990 mgm. H_2SO_4/100 gm. The acetyl was determined by a standard method (6). The cellulose acetate sulphate was kept in a large volume of water until required.

Cellulose Acetate Sulphate (Fibrous Process, Batch No. 28)

The preparation is similar to U.S. Patent 2,143,332 (by Sindl and Frank (14)). Cellulose (80 gm., 1 part) was treated with 99.5 acetic acid (960 gm., 12 parts) for 12 hr. The excess of liquid was then removed by centrifuging until the weight of the mass was 2.4 parts (192 gm.)

Acetylation was effected by a mixture, preliminarily cooled to 5°C., consisting of benzene (704 gm., 8.8 parts), acetic acid (160 gm., 2.0 parts), acetic anhydride (240 gm., 3.0 parts), and sulphuric acid (12.8 gm., 0.16 parts). The temperature was allowed to rise gradually to 25°C. After 24 hr., the fibrous acetate was soluble in acetone and in a mixture of methylene chloride (9 parts) and alcohol (1 part).

The acetylation medium was removed by centrifuging. The product was washed twice with benzene, once with ethyl alcohol, and repeatedly with distilled water. Analysis: apparent acetyl, 38.5%; sulphate, 2876 mgm. H_2SO_4/100 gm. After ion exchange with calcium, the analysis (for calcium) showed 1.00 equivalent of acidity for each sulphate group.

Determination of Sulphate

The method used was a modification of that developed by Dunnicliff (5) for the determination of sulphate in nitrocellulose. While the method is long and tedious it is capable of good precision and accuracy. A sample of 2 to 3 gm. (dry weight) was weighed and transferred to a 400 ml. tall beaker. Concentrated nitric acid (25 ml.) was added so as to wet the sample thoroughly. The beaker was covered with a watch glass, and the contents boiled gently on a hot plate. When the evolution of brown fumes subsided, small portions of potassium chlorate were added periodically until the liquid became a pale yellow; a total of 1 gm. of potassium chlorate was usually adequate. The contents of the beaker were then evaporated to dryness and the beaker removed from the hot plate. Nitric acid (25 ml.) followed by potassium chlorate (about 0.5 gm.) was added and the contents again evaporated to dryness. If the residue was not then white in color, the process was repeated. Concentrated hydrochloric acid (25 ml.) was added to the beaker and the contents evaporated to dryness. To ensure the complete removal of nitric acid the process was repeated with another 25 ml. portion of hydrochloric acid. The residue was dissolved in water and filtered through fast filter paper. The filtrate and washings were diluted with water to 200 ml., 2 drops of concentrated hydrochloric acid added, and the mixture heated to boiling in a 200 ml. covered beaker. Ten per cent barium chloride solution (10 ml.) was added drop by drop with constant stirring. Boiling was continued for a few minutes and the beaker placed on top of an oven at 100°C. for six hours. The precipitate was collected in a tared porous-bottom porcelain crucible, heated in a muffle furnace at 800°C. for one hour, cooled in a desiccator, and reweighed.

Determination of Calcium

The method was similar to that developed by Schwarzenbach *et al.* (13) for the determination of water hardness and is based on the formation of a

soluble chelate with ethylenediaminetetraacetic acid (EDTA) at a pH of 10, the end point being detected by the formation of a colored complex between EDTA, magnesium, and the azo dye eriochrome black. Organic material was first destroyed by digestion with nitric acid and potassium chlorate as described above, and the residue dissolved by warming with distilled water (200 ml.). When larger amounts of calcium sulphate were present, it was sometimes necessary to use a greater volume of water. The resulting solution was neutralized and then buffered by adding 30 ml. of a solution containing 67.5 gm. ammonium chloride and 570 ml. of concentrated ammonia in 1 liter. Eight drops of indicator solution (0.5 gm. of eriochrome black in 50 ml. of triethanolamine) were added and the solution titrated with a solution containing 9.5 gm. of the disodium salt of ethylenediaminetetraacetic acid, 0.1 gm. of anhydrous magnesium chloride, and 0.5 gm. of caustic soda to the liter. The EDTA solution was standardized against a calcium chloride solution containing exactly 1 mgm. of calcium per ml. The indicator solution was prepared by the method proposed by Diskant (3).

Determination of Sodium

A weighed sample (about 1 gm.) was transferred to a 125 ml. Erlenmeyer flask and digested with concentrated nitric acid (15 ml.) on a steam plate until a clear amber-colored solution was obtained. Concentrated sulphuric acid (1 ml.) was added and digestion continued until sulphur trioxide fumes were evolved. Concentrated nitric acid was added drop by drop until all carbonaceous matter had decomposed. The flask was removed from the hot plate, washed down with distilled water, and again heated until evolution of sulphur trioxide almost ceased. The solution was allowed to cool and was made up to 100 ml. Five milliliters of the solution was used for the sodium estimation in the Beckman Model DU Spectrophotometer with the Model 9200 flame attachment. The sodium content was first estimated from the standard curve for the instrument prepared over the range 0 to 200 parts per million of sodium from standard solutions of sodium which were prepared from a master solution containing 5012 parts per million of sodium. All standard solutions were stored in polythene bottles to prevent contamination. The sodium concentration was then determined more accurately by comparing the flame intensity with that of two standard solutions containing respectively slightly less and slightly more sodium and differing in sodium concentration from the unknown by not more than 15 parts per million. The exact sodium concentration was determined by interpolation using the formula:

$$x = A + \frac{(B - A)\,(I_x - I_A)}{(I_B - I_A)}$$

where x = concentration of sodium in the unknown,

A = concentration of sodium in the standard of lower concentration,
B = concentration of sodium in the standard of higher concentration,

I_A = flame intensity of A in transmission dial units,
I_B = flame intensity of B in transmission dial units,
I_x = flame intensity of x in transmission dial units.

The procedure used with the flame photometer was similar to that described in Beckman bulletin 259A. The instrument settings used were:

Selection switch	0.1
Wave length	589 mμ
Slit	0.10 mm.

The average of five separate transmission dial readings was taken when calculating the exact sodium content.

Hydrolysis of Cellulose Acetate Sulphate

A sample of about 15 gm. was shaken with 250 ml. of distilled water at room temperature and allowed to stand for 2 to 14 days depending on the time the original batch had been in contact with water without change. The water was removed and the sample washed, the filtrate and wash water being discarded. The sample was then treated with distilled water for 24 hr., filtered, and washed with three lots of 75 ml. of distilled water. The filtrate and the washings were made up to 500 ml. Sulphate was determined turbidometrically (11) and total acidity by titration with 0.01 N sodium hydroxide, using phenolphthalein as indicator. Acetic acid was calculated by difference.

Drying Samples and Determining Moisture Content

The material was dried at room temperature in an evacuated chamber through which a slow stream of dry air was continuously bled. The initial drying was effected by the use of a water aspirator which maintained a vacuum of about 20 mm. with an air flow of one bubble per second. After the removal of the bulk of the moisture, the water aspirator was replaced by a high vacuum pump and drying was continued until constant weight was attained. Several samples (20 gm. damp weight) could be dried in about 24 hr. The equipment consisted of a vacuum chamber (Cenco # 95056) fitted with a needle valve to control the rate of air admitted and with a vacuum gauge to determine the degree of evacuation. The air entering the chamber was dried by passage through an absorption bottle containing sulphuric acid and a drying tower of calcium chloride.

Stability Test

Air, dried and free of carbon dioxide, was passed over the dry sample (0.5 gm.) which was maintained at 65° ± 0.5°C. The volatile decomposition products were carried by the air into the indicator solution. The time lapse between the insertion of the sample and the appearance of the first blue in the indicator solution was recorded as the stability test time. The apparatus is shown in Fig. 4 and consisted of a constant-temperature block in which U-shaped sample tubes were located. The sample tube was connected by means of a ball joint to the indicator tube containing the indicator solution (1 ml.). The air passing over the sample was first passed through towers containing respectively calcium chloride and soda lime. The flow of air was

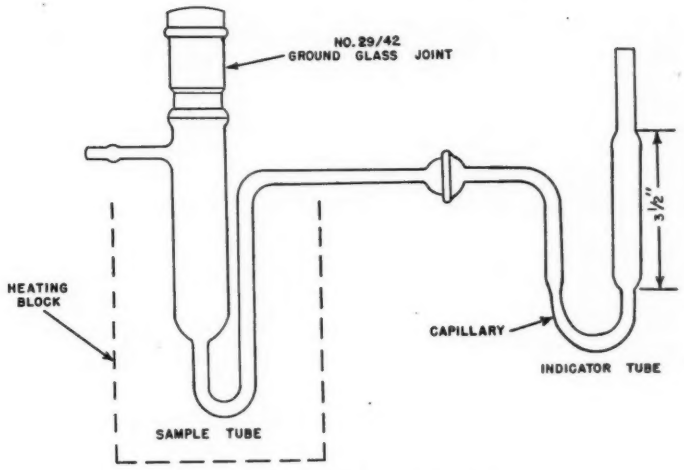

FIG. 4. Apparatus for stability test.

50 bubbles per minute. A sintered glass disk was placed in the line to smooth out the air flow.

The indicator solution contained 20 ml. of each of the following stock solutions: (1) potassium iodide solution (2 gm./100 ml.), (2) potassium iodate solution (1 gm./100 ml.), (3) sodium thiosulphate (0.001 *N*) and 10 drops starch solution (0.5%). The stock solutions were prepared from carbon-dioxide-free water. Ion-free water from a Barnstead Demineralizer was found convenient. Fresh indicator was prepared each day and kept in a brown bottle.

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EFFECT OF GELATIN ON THE CHANGES IN INITIAL CATHODE POLARIZATION DURING ELECTRODEPOSITION OF COPPER[1]

By B. I. Parsons[2] and C. A. Winkler

ABSTRACT

In the absence of addition agent, the cathode polarization during initial electrolysis of copper from a solution of acid copper sulphate rose almost instantaneously from zero to approximately the steady state polarization. When gelatin was present in the electrolyte, the polarization generally increased to a maximum, P_{max}, (in time t_{max}) then decreased to a minimum, P_{min}, (in time t_{min}) beyond which it increased to the steady state value, P_s. Generally, P_{max} increased to a steady value with an increase in the time, T_0, the electrode was in contact with the electrolyte before electrolysis was begun. At low, moderate, and high current densities respectively, t_{max} increased continuously, passed through a maximum, and decreased continuously with T_0. The behavior of t_{min} approximately paralleled that of t_{max}. The polarization was linear in the logarithm of the current density; t_{max} and t_{min} decreased with increase in current density. The polarization values increased and t_{max} decreased, with increase in gelatin concentration. Increase of temperature had approximately the same effect as decrease in current density. With both chloride and gelatin present, P_{max} was practically independent of T_0 and chloride concentration, while P_{min} and P_s showed minimum values at about 2 mgm./l. chloride.

INTRODUCTION

Previous studies have shown that, during electrodeposition of copper in a Haring cell, the cathode polarization generally changes until a steady state value is reached (1, 2). This steady state polarization is increased when gelatin is present in the electrolyte (3). These observations, originally made in cells that permitted convection currents upward past the cathode face, have been substantiated in convection-free systems (7).

A cathode-ray oscillograph has now been used to study the effect of gelatin on the initial, rather than on the steady state polarization, under a variety of conditions. The experimental results obtained are recorded in the present paper.

EXPERIMENTAL

Experiments have been made in both a standard type (horizontal) Haring cell (1) and in the modified (vertical) cell in which convection currents are eliminated (6). Each type of cell contained 150 ml. of air-saturated electrolyte, and in each the apparent area of electrode surface immersed was 10 cm.^{2} Steady or slowly changing potentials were measured with a Leeds and Northrup type K2 potentiometer. The rapidly changing initial potentials were obtained with either a DuMont 304-H cathode-ray oscilloscope or a Brush BL932-BL201 recording oscillograph. The copper sulphate and sulphuric acid were reagent grade, the water was twice distilled, and the gelatin was U.S.P.

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Contribution from the Physical Chemistry Laboratory, McGill University, with financial assistance from the National Research Council of Canada.
[2] *Holder of a National Research Council Fellowship.*

grade. Gelatin solutions, prepared at room temperature, were used within 30 hr.

A standard surface was obtained on each cathode before it was used, by electrodeposition on it at 25°C. from a standard electrolyte (125 gm. $CuSO_4 \cdot 5H_2O$ and 50 ml. conc. H_2SO_4 per liter of solution) at an apparent current density of 3 amp./dm.^{2} for 30 min., followed by 2 amp./dm.^{2} for one hour. The polarization at the end of this time was 110 ± 5 mv.

The cells and solutions were brought to the desired temperature in a suitable thermostat. The standard surface was laid down on the cathode in one cell, after which the electrode assembly was quickly transferred to another cell containing the electrolyte to be examined. The immersion time, T_0, is defined as the time the electrode was in contact with the electrolyte before current was passed. The cathode compartment of the Haring cell was connected to the oscillograph before the current was turned on. After the initial rapid changes of potential had been determined with the oscillograph, deposition was continued and the change of potential to the steady state followed with the potentiometer. The level of reproducibility in the various experiments to be discussed was generally the order ± 5%.

RESULTS

General Observations

When current was passed in the absence of addition agent the polarization increased almost instantaneously to about 100 mv., then changed more slowly

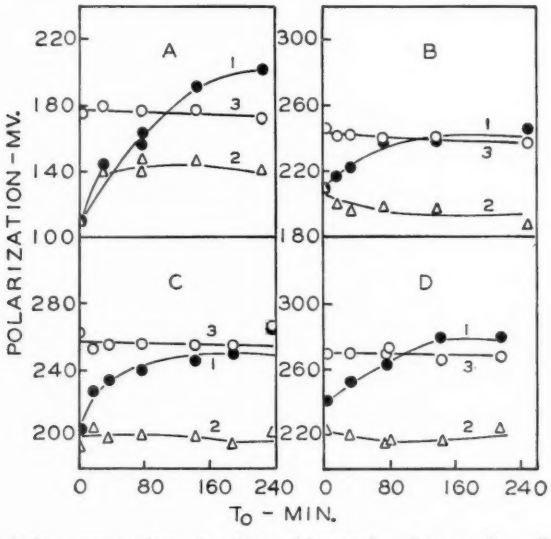

FIG. 1. Typical curves to show the effect of immersion time on P_{max}, P_{min}, and P_s, at different gelatin concentrations. Current density 2 amp/dm.^{2}; temperature 25°C. Curves 1—P_{max}, 2—P_{min}, 3—P_s.
A—1, B—10, C—25, D—100 mgm. gelatin/liter of standard electrolyte.

to the steady state value. However, when gelatin was present in the electrolyte, the polarization generally increased rapidly to a maximum, then decreased to a minimum, beyond which it again increased slowly to the steady state polarization characteristic of the gelatin concentration. For convenience the polarization maximum is designated as P_{max}, the minimum as P_{min}, the steady state polarization as P_s, the time required to attain P_{max} as t_{max}, and the time to attain P_{min} as t_{min}. The observations in the absence of addition agent were independent of T_0 but in the presence of gelatin there were changes in the initial polarization pattern as T_0 was altered.

The Effect of Gelatin

Changes were observed in the polarization pattern with changes in immersion time, gelatin concentration, current density, and temperature. The curves in Fig. 1 are typical for the changes in P_{max}, P_{min}, and P_s with T_0 at different gelatin concentrations. Relations of the same general type were obtained between these quantities when the current density and temperature were varied, although there were differences in matters of detail. For example,

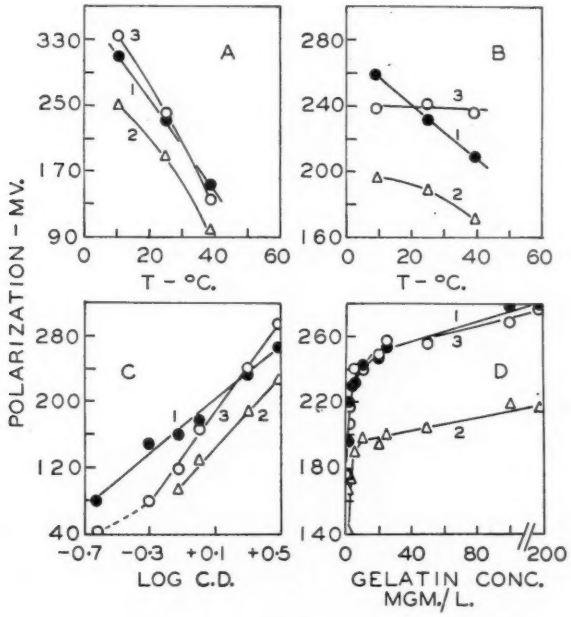

FIG. 2. Summary of the effect of temperature, current density, and gelatin concentration on P_{max}, P_{min}, and P_s. $T_0 > 75$ min. Curves 1: P_{max}; 2: P_{min}; 3: P_s.

A. Immersion and deposition at temperature plotted.

B. Immersion at temperatures plotted, electrode then transferred to electrolyte at 25°C. and deposition begun at that temperature after 2 min.

For both A and B, gelatin concentration = 5 mgm./l., current density = 2 amp./dm.^{2}

C. Effect of current density. Temp. = 25°C., gelatin concentration = 5 mgm./l.

D. Effect of gelatin concentration. Temp. = 25°C., current density = 2 amp./dm.^{2}

the relative positions of the three curves were altered by suitable changes in current density and temperature, while at sufficiently low current densities (<0.5 amp./dm.^{2}) no minimum at all appeared in the potential–time curve. The influence of the various factors on the potential values may be summarized as in Fig. 2, for values of T_0 (generally >75 min.) where the potential values become practically constant.

The changes in t_{max} and t_{min} with T_0, at different gelatin concentrations, are shown in Fig. 3, as further indication of the reasonably systematic behavior of the initial polarization pattern with alteration of the conditions of

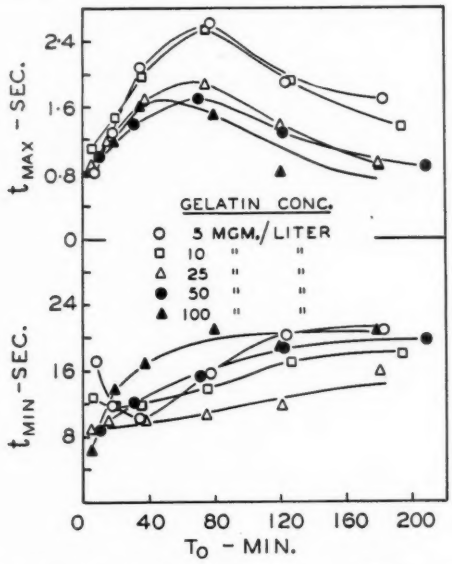

FIG. 3. Effect of immersion time on t_{max} and t_{min}, at different gelatin concentrations. Current density 1 amp./dm.^{2} Temp. 25°C.

electrolysis. The analogous curves at different current densities are shown in Fig. 4. Curves for the effect of temperature on t_{max} and t_{min} are not reproduced but the results may be briefly summarized. With immersion and deposition (2 amp./dm.^{2}, 5 mgm./l. gelatin) at 37°C., t_{max} passed through a maximum (*ca.* 6 sec.) at $T_0 = 80$ min., while t_{min} increased steadily from about 20 sec. at $T_0 = 15$ min. to 55 sec. at $T_0 = 180$ min. A maximum in t_{max} (at 2.5 sec.) was also observed at 25°C. when T_0 was about 80 min., while at this temperature t_{min} passed through a slight minimum (at 10 sec.) for $T_0 = 40$ min. and became essentially constant at 20 sec. for $T_0 > 120$ min. At 10.5°C., t_{max} was much decreased. Both t_{max} and t_{min} showed little change from the values 0.5 sec. and 9 sec. respectively with increase of T_0.

Preliminary experiments showed that the absolute values of P_{max} and P_{min} depended upon the method of dissolving the gelatin. The value of P_{max} and P_{min} decreased with

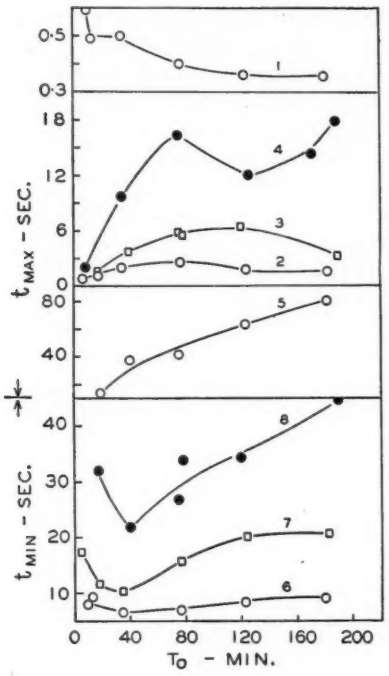

FIG. 4. Effect of current density on t_{max} and t_{min}. Gelatin conc. 5 mgm./l. Temp. 25°C.

CURVE NO.	CURRENT DENSITY (amp./dm.²)
1, 6	2
2, 7	1
3, 8	0.75
4	0.50 (No minimum observed)
5	0.25 (No minimum observed)

(*a*) an increase in the age of the electrolyte containing gelatin,

(*b*) an increase in the temperature at which the gelatin solution was prepared.

Extremes in either factor also lowered the steady state polarization.

The effect of molecular weight of the gelatin on the polarization pattern was studied in two ways. Fractionation of the stock gelatin by coacervation (5) gave two portions of molecular weights* 94,500 and 14,500, while average molecular weights ranging from 55,000 to 9,500 were obtained by degrading a 1% gelatin solution at 100°C. for various lengths of time. Except for small changes in the absolute potentials there was little alteration of the initial polarization pattern with a change in the molecular weight of the gelatin.

The effect of the cathode surface on the polarization pattern was also investigated with two types of surface other than the standard. One of these

**The molecular weight of the gelatin was determined by using the relation between the intrinsic viscosity and the molecular weight established by Pouradier and Venet (5) $N = 1.66 \times 10^{-5} M^{0.885}$.*

was the base metal of the copper stock after it had been etched in 50% nitric acid. The other was the base metal ground with 120 mesh emery powder. The ground surface was allowed to stand in standard electrolyte for several hours before the experiment was begun.

Whereas with the standard deposited surface the build-up in potential to P_{max} could actually be observed, the polarization at the etched surface in the presence of gelatin showed only a rapid decrease to P_{min} from some higher value, followed by a slow increase to P_s. The initial high value of the potential increased with T_0 in a manner similar to that observed for P_{max} on a deposited surface. Experiments in the absence of gelatin showed no such potential pattern. At 2 amp./dm.^{2} and 25°C. the initial potential observed was approximately 65 mv. and this increased to a P_s value of 100 mv.

The immersion time for the ground surface was varied from 9 to 850 min. At 2 amp./dm.^{2} and 25°C. the polarization in the absence of addition agent rose instantaneously to about 60 mv., then continued to rise slowly towards P_s. The initial polarization pattern observed in the presence of gelatin was exactly the same as that observed in its absence.

To determine whether the observations recorded above were in any way peculiar to the Haring Cell, polarization measurements on a standard surface were made with a probe assembly at 25°C. and 2 amps./dm.^{2} The results paralleled those obtained in the Haring cell, both in the presence and absence of gelatin.

Stirring the electrolyte in the cathode compartment during T_0 exaggerated the deviations of the experimental points from a smooth curve, but the difference between P_{max} and P_{min} still increased as T_0 was increased.

For the experiments in the absence of convection, it was not convenient to prepare the cathode surface by deposition in a separate cell, as in the previous experiments. The same electrode and electrolyte were therefore used throughout and the standard surface was the deposited surface of the previous experiment.

Initially the cathode was etched with 50% nitric acid, rinsed, and placed at the top of the cell. Current was passed until the measured polarization indicated that hydrogen was being evolved. The flow of current was then stopped and the electrolyte mixed by tipping and turning the cell. The immersion time was measured from this time of mixing.

The initial polarization pattern observed in the presence of gelatin with the vertical cell at 0.5 amp./dm.^{2} was similar to the pattern observed with the horizontal cell at 2 amp./dm.^{2} The polarization rose to P_{max}, fell to P_{min}, then slowly increased until hydrogen evolution occurred. An increase of the current density to 2 amp./dm.^{2} in the vertical cell did not change the polarization pattern.

The Effect of Chloride and Gelatin

The steady state polarization measured in an electrolyte containing gelatin is lowered considerably by the addition of a small amount of chloride ion (4). As the amount of chloride is further increased, the polarization again in-

creases. It was obviously of interest to determine whether this behavior might be reflected in the initial polarization values.

The effect of chloride on the initial polarization pattern in the absence of gelatin and in the presence of gelatin is shown in Fig. 5. The chloride ion was introduced into the standard electrolyte from a concentrated sodium

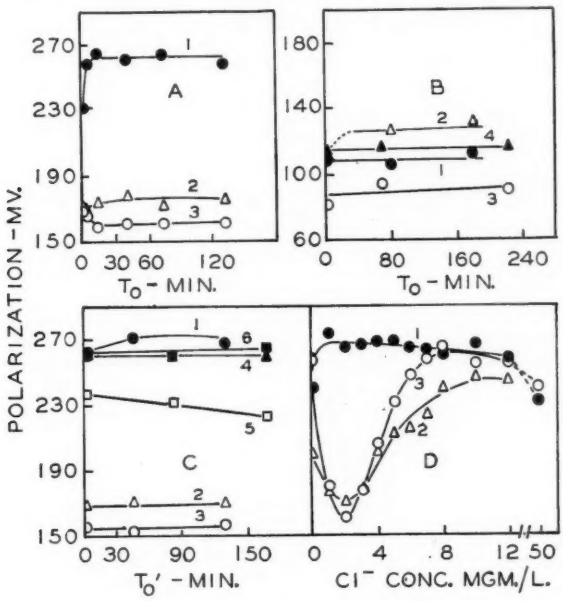

FIG. 5. The effect of chloride on the initial polarization pattern. Current density 2 amp./dm.² Temp. 25°C.

Parts A, C, and D.— Curves 1, 4: P_{max}; 2, 5: P_{min}; 3, 6: P_s.

Part B.—Curves 1, 3: first recorded polarization; 2, 4: P_s.

A. The effect of the immersion time on the polarization pattern. Gelatin concentration: 25 mgm./l. Chloride ion concentration: 2 mgm./l.

B. The effect of chloride in the absence of gelatin. Curves 1, 2: 2 mgm./l. chloride; 3, 4: 10 mgm./l. chloride.

C. The effect of immersion in electrolyte containing 25 mgm./l. gelatin for 75–80 min., then immersion in electrolyte containing both gelatin and chloride for the specified period of time. Curves 1, 2, 3: 2 mgm./l. chloride; 4, 5, 6: 10 mgm./l. chloride.

D. The effect of chloride concentration on the initial polarization pattern. Gelatin concentration: 25 mgm./l. Immersion time: 75–80 min.

chloride stock solution. The effect of the immersion time on the initial polarization pattern in electrolytes containing both gelatin and chloride was determined in two series of experiments. In the first the prepared cathode was transferred, in the usual way, to the Haring cell containing the electrolyte to be examined. After the specified immersion period the current was turned on and the initial polarization recorded. In the second series the cathode was immersed for 75–80 min. in electrolyte containing 25 mgm./l. gelatin, then transferred to the test cell containing gelatin and chloride for further immersion, T_0, before deposition was begun.

While the addition of chloride to electrolyte containing gelatin had a profound effect on the P_{max}–T_0 relation, the most interesting feature of the results is perhaps that, at long immersion times, P_{max} was virtually uninfluenced by chloride ion concentration, whereas both P_{min} and P_s passed through minima corresponding to that observed for P_s in the earlier studies (4).

ANODE POLARIZATION

The polarization pattern at the anode was also observed to reflect the presence of gelatin in the electrolyte.

The standard surface chosen for the anode was the base metal of the copper stock. Initially, the anode was brought to red heat in an oxygen flame, then etched deeply with 50% nitric acid. The final surface was prepared by anodic solution into the electrolyte containing gelatin at 25°C. and 2 amp./dm.^{2} Experiments were made in succession upon the same electrode.

The polarization pattern observed with gelatin-free electrolyte was similar to that obtained in the cathode compartment. The anode polarization at 25°C. and 2 amp./dm.^{2} was observed to rise from zero to approximately 35 mv. within 0.02 sec., and to remain at approximately this value as solution of the anode continued. The immersion time had no effect on the measured quantities.

When the electrolyte contained gelatin the initial anode polarization decreased from a very high value to an essentially steady state value within 0.25 sec. The magnitude of the first polarization value it was possible to record increased with immersion time, from 68 mv. at $T_0 = 2$ min. to 100 mv. at $T_0 = 20$ min., and then remained practically constant with further increase of T_0. The steady state anode polarization showed a slight increase from 50 mv. at $T_0 = 2$ min. to 56 mv. at $T_0 = 10$ min., at which value it remained constant with further increase of T_0.

DISCUSSION

The results of the present study demonstrate a sensitive and reasonably systematic behavior of the initial polarization pattern with changes in conditions of electrodeposition in the presence of gelatin. Preliminary work with other addition agents has indicated that gelatin is not unique in modifying the changes in initial polarization and that the changes observed with different addition agents are of various types. It may be expected, therefore, that further studies of such patterns should be useful in interpreting the action of addition agents generally.

The dependence of P_{max} and t_{max} on T_0 serves to emphasize the processes that occur when the cathode is immersed in the acid electrolyte containing gelatin, and before current is passed. These processes are presumably corrosion and adsorption, and it seems reasonable to suppose that after sufficiently long immersion times, a steady state is attained in respect of these two processes. While adsorption of gelatin, as such, probably occurs, the formation of complexes with cupric and cuprous ions formed during the corrosion process, and their subsequent adsorption might also be important. It is hoped that

some indication of the part played by copper ion – gelatin complex formation might be obtained from a study with simple amino acids, now in progress in this laboratory.

It is not proposed to attempt a detailed explanation of the results obtained in the present study, since an unequivocal interpretation has yet to be found for the mere existence of the observed maxima and minima in the polarization–time curves. Even a tentative explanation of these seems to require that, since P_{max} depends upon T_0, it depends upon the extent to which the electrode surface is covered with gelatin (or copper–gelatin complex), and that this, in turn, is related to the extent that gelatin is depleted in the vicinity of the cathode when deposition is begun. Thus, for relatively large extent of uncovered surface, corresponding to relatively small values of T_0, the supply of gelatin adjacent to the cathode might be considerably depleted when the current is switched on, while the reverse argument would apply for larger T_0 values.

The mechanism by which gelatin might suffer such depletion is not known. It could conceivably involve complex formation with cuprous ions at the cathode surface, or it might be due merely to adsorption on uncovered or newly deposited copper surface, perhaps accentuated by the negative charge on the cathode. Replenishment of gelatin at the cathode–electrolyte interface would be mainly by convection, and should have little influence on the polarization pattern during the initial changes. Eventually, of course, a steady state should be established between the rates at which gelatin is brought up to, and used up at the cathode.

On the basis of the preceding ideas, serious depletion of gelatin might be expected in the immediate neighborhood of a freshly prepared cathode, with its relatively large amount of uncovered surface, when it is immersed in electrolyte containing gelatin and the current turned on after a short interval, i.e. small T_0 value. Hence, the initial rise of potential due to the action of the addition agent should be followed by a tendency for the potential to decrease as deposition is continued in an environment impoverished of gelatin. Accordingly, a maximum in the potential–time curve might be expected. Obviously, the more the electrode is covered with addition agent before the current is turned on, i.e. the larger the T_0 value, the less initial depletion of gelatin there should be at the cathode–solution interface. Hence, with increase of T_0 the values of both P_{max} and t_{max} should tend to increase, since the initial potential increase should continue longer and to higher values before depletion of gelatin at the newly deposited surface reverses the trend. This type of behavior was observed at low current densities, but an optimum or slight decrease in t_{max} with increased T_0 was observed at higher current densities. It is possible, however, that the different relations between t_{max} and T_0 at different current densities simply reflect the different ways in which gelatin depletion is related to the extent of uncovered surface after T_0 and to deposition of new surface. As indicated previously, larger values of T_0 should correspond to less depletion, hence larger t_{max}, while higher current densities, with concomitant higher rates of deposition of new surface, might correspond to

more rapid depletion, hence smaller t_{max}. Appropriate combinations of T_0 and current density conditions might permit the observed range of t_{max}–T_0 relations.

The existence of P_{min}, following P_{max}, can also be accounted for, since gradual establishment of convection past the cathode face should increasingly replenish the gelatin supply and cause a gradual increase of potential again, until the steady state is reached.

The tentative interpretation given above is limited to a few outstanding features of the present results. Its extension to other observations made during the study might be offered, but before this is done it would seem that an attempt should be made to get experimental verification of the ideas involved, particularly with other addition agents.

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A NOTE ON THE USE OF INDIUM FOR REMOVAL OF MERCURY VAPOR IN VACUUM SYSTEMS[1]

By R. D. Heyding and E. A. Flood

ABSTRACT

It is shown that metallic indium adsorbs mercury vapor quite rapidly after a short induction period. It is suggested that indium may be found useful in removing traces of mercury vapor from vacuum systems.

In vacuum systems requiring low mercury vapor concentrations, the conventional liquid-air cooled trap between the system and sources of mercury vapor is often replaced by a trap containing a mercury vapor 'getter', e.g., metallic sodium, gold, or cadmium. Similarly, gold and brass are extensively used in traps into which vapors are condensed, prior to distillation into a weighing vessel, to minimize the transport of mercury into the weighing vessel.

During the course of another investigation, we observed that metallic indium has a considerable affinity for mercury vapor, and we have subsequently made a cursory study of the relative rates of absorption of mercury vapor by several metallic foils.

Small foils of gold, indium, and aluminum (all 99.95% pure) and brass (67% Cu, 33% Zn) were prepared by rubbing with fine emery paper and washing with alcoholic potassium hydroxide and water. The grade of emery paper employed appeared to have little effect on the absorption of mercury vapor when expressed in milligrams per planar square centimeter. The foils were suspended individually on a quartz spiral about 10 cm. above a pool of mercury, and the increase in weight *in vacuo* observed, using a cathetometer in the usual manner. While such an apparatus will not register the absorption of the first few molecular layers, increments of 0.1 mgm. $cm.^{-2}$ could be detected.

At room temperature (25°C.), the absorption of mercury vapor by brass and aluminum foils in 100 hr. was negligible. Indium was found to absorb more readily than gold; this was particularly evident at higher 'surface concentrations'.

Rates of absorption, mgm. $cm.^{-2}hr.^{-1}$

	Surface Concentrations		
	Ca. zero	*Ca.* 5 $mgm.cm.^{-2}$	*Ca.* 8 $mgm.cm.^{-2}$
Gold	0.4	0.02	—
Indium	5.0	2.0	0.6

Spicer and Banick (1) have recently shown that indium amalgams containing 18 to 42% mercury have a liquidus as well as a solidus phase. The

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formation of this liquidus phase on absorption of mercury vapor led to perforation of the foil and, of course, disintegration if the absorption was allowed to proceed. We have prepared a more rigid 'getter' by electrodeposition of indium from the sulphate on fine brass gauze at high current densities. The rate of absorption of mercury vapor by the gauze was comparable to that by the foil, and the droplets of amalgam were retained by the brass.

Unlike gold, indium foil, regardless of preparation, required four to five hours *in vacuo* before absorption began unless some procedure was employed to make an initial deposition of mercury on the surface. Admission of air to the system during absorption imposed a similar induction period before absorption was resumed. Since admission of water vapor or nitrogen to the system did not give this effect, it is attributed to the formation of an oxide film over the foil.

The value of indium as a mercury 'getter' will be a function of the mercury vapor pressure of the amalgams formed on absorption. We have attempted to measure the vapor pressures of amalgams containing less than eighteen per cent mercury (i.e., solidus phase only) by the effusion method, and have found these to be less than 5×10^{-7} mm. Hg, i.e., probably less than a thousandth of that of mercury vapor at room temperature (25°C.). The rate of desorption of mercury from indium foil by a liquid-air cooled trap was found to be less than 0.008 mgm. $cm.^{-2}$ hr^{-1}.

Thus one would expect that under most of the ordinary laboratory conditions indium should be better than gold for removing traces of mercury vapor from vacuum systems. The relatively low cost of indium and the ease with which it can be molded into various shapes, electrodeposited, etc., are also to be borne in mind. It may be remarked that indium adheres tenaciously to glass and consequently castings cannot be removed from glass tubes unless the tubes were previously well oiled.

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THE REACTIONS OF METHYL AND ETHYL RADICALS WITH DIETHYL KETONE[1]

By P. Ausloos[2] and E. W. R. Steacie

ABSTRACT

The hydrogen-abstraction reactions of methyl and ethyl radicals from diethyl ketone have been studied in the temperature range 25 to 160°C. Azomethane and azoethane were used as photochemical sources of methyl and ethyl radicals. The activation energies found were 7.0 and 7.6 kcal., respectively, for the reactions:

$$CH_3 + C_2H_5COC_2H_5 \rightarrow CH_4 + C_2H_4COC_2H_5 \quad [1]$$

$$C_2H_5 + C_2H_5COC_2H_5 \rightarrow C_2H_6 + C_2H_4COC_2H_5. \quad [2]$$

If the combination of both methyl and ethyl radicals is assumed to occur at every collision, the steric factors for the two reactions are $E_1 = 7.4 \times 10^{-4}$, $E_2 = 7.1 \times 10^{-4}$.

INTRODUCTION

Studies of the photolysis of azomethane (2) and of azoethane (1) have shown that these compounds may be used as sources of methyl and ethyl radicals for the investigation of hydrogen-abstraction reactions of the type:

$$CH_3 + RH \rightarrow CH_4 + R \quad [3]$$

and

$$C_2H_5 + RH \rightarrow C_2H_6 + R. \quad [4]$$

One advantage of the use of azo-compounds in this way is that they may be photolyzed by light of wave length greater than 3400 Å, where ketones and most other organic compounds are transparent. Azo-compounds may therefore be photolyzed in their presence without complications due to the simultaneous photolysis of the substances under investigation.

It appeared to be of interest to investigate the reaction of methyl and ethyl radicals with diethyl ketone. In the first place this serves as a check on the values found for the reaction

$$C_2H_5 + C_2H_5COC_2H_5 \rightarrow C_2H_6 + C_2H_4COC_2H_5 \quad [2]$$

in the photolysis of diethyl ketone itself (3), and in addition it gives an opportunity to investigate the effect of substituting methyl for ethyl radicals, and thus comparing the rates of reactions [3] and [4] for the same substance, RH.

EXPERIMENTAL

Azomethane and azoethane were prepared by Dr. Leitch of this laboratory (4). Diethyl ketone was obtained from Eastman Kodak Co. All compounds were distilled *in vacuo* before use.

The light source was a Hanovia S500 medium pressure mercury arc. The apparatus was essentially similar to that used in previous papers from this laboratory. The fused quartz reaction vessel was a cylinder, approximately

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Contribution from the Division of Pure Chemistry, National Research Council, Ottawa, Canada. Issued as N.R.C. No. 3273.
[2]*National Research Council of Canada Postdoctorate Fellow, 1952–54.*

5 cm. diameter and 10 cm. long. It was completely filled by a parallel light beam. Two types of filter were used to limit the incident radiation to longer wave lengths:

(*a*) A Corning violet ultra No. 7-37, or 586, 6 mm. in thickness, which was opaque at wave lengths below 3150 Å.

(*b*) A Corning filter No. 0-52, or 738, opaque at wave lengths below 3400 Å.

The analytical section of the apparatus was the same as that described elsewhere (1). The $N_2 - CH_4$ fraction was removed at $-195°C.$, and the $C_2H_6 - C_2H_4$ fraction at $-170°C.$ Repeated cooling and heating was necessary to separate butane from azoethane at $-125°C.$ The $N_2 - CH_4$ and $C_2H_6 - C_2H_4$ fractions were analyzed with a mass spectrometer. To avoid complications due to secondary reactions the amount of conversion of azoethane was always kept below five per cent.

RESULTS AND DISCUSSION

(*A*) *The Reaction of Methyl Radicals with Diethyl Ketone*

When azomethane is photolyzed in the presence of diethyl ketone, the following steps in the mechanisms of their respective decompositions have to be taken into account

$$CH_3N_2CH_3 + h\nu \rightarrow 2CH_3 + N_2 \qquad [5]$$

$$CH_3 + CH_3 \rightarrow C_2H_6 \qquad [6]$$

$$CH_3 + CH_3N_2CH_3 \rightarrow CH_4 + CH_2N_2CH_3 \qquad [7]$$

$$CH_3 + C_2H_5COC_2H_5 \rightarrow CH_4 + C_2H_4COC_2H_5 \qquad [1]$$

$$C_2H_4COC_2H_5 \rightarrow C_2H_4 + CO + C_2H_5. \qquad [8]$$

If reaction [8] is omitted, a steady-state treatment gives:

$$k_1/k_6^{\frac{1}{2}} = (R_{CH_4}/R_{C_2H_6}^{\frac{1}{2}} - k_7/k_6^{\frac{1}{2}}[CH_3N_2CH_3])/[C_2H_5COC_2H_5].$$

Reaction [8] does not seem to occur to any appreciable extent in the temperature range $25 - 150°C.$, especially at the rather high intensities used in this work. This was confirmed by the fact that at $150°C.$ no measurable amount of CO_2 could be detected in the N_2 fraction after it had been passed over hot cuprous oxide. Also, less than one per cent of C_2H_4 was present in the $C_2H_6 - C_2H_4$ fraction.

The values of $k_7/k_6^{\frac{1}{2}}$ which are required in the calculations have been taken from an experimental Arrhenius plot for azomethane alone. For runs with three different samples of azomethane no curvature in the plot could be found in the low temperature region, contrary to previous work (2). The best line through the points was

$$k_7/k_6^{\frac{1}{2}} = 8.5 \times 10^{-9}\, e^{-7300/RT} \text{ cm.}^{3/2} \text{ molecule}^{-\frac{1}{2}} \text{ sec.}^{-\frac{1}{2}}$$

The results for $k_1/k_6^{\frac{1}{2}}$ are given in Table I. In Fig. 1, $\log k_1/k_6^{\frac{1}{2}}$ is plotted against $1/T$. An activation energy of 7.0 ± 0.1 kcal. for reaction [4] is obtained from the slope of the curve, if the activation energy for the recombination of two methyl radicals is assumed to be zero. There is again no curvature in this plot at low temperatures. The cause of curvature in such plots will be

TABLE I
REACTION OF METHYL RADICALS WITH DIETHYL KETONE

Temp., °K.	Pressure, cm.		$R_{CH_4} \times 10^4$, cc./min.	$R_{C_2H_6} \times 10^4$, cc./min.	$k_1/k_6^{\frac{1}{2}} \times 10^{13}$, cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$
	Azomethane	Diethyl ketone			
Filter 586					
299	5	1.6	1.98	26.8	2.45
301	4.07	1.5	1.54	20.1	2.4
313	2.85	1.93	1.19	4.67	3.69
315	1.4	1.16	0.56	3.22	3.74
326	3.97	1.45	3.38	16	6.5
330	3.46	1.89	3.62	12	7.25
331	2.16	1.73	1.61	3.7	6.9
354	2.18	2.06	2.55	1.5	15
361	3.78	1.67	6.21	8.55	16.6
407	4.11	1.5	11.06	3.64	56
Filter 738					
370	3.06	1.86	7.39	5.93	23.1
387	2.96	2.42	10.35	4.23	34.7
406	3.24	1.87	10.29	2.59	55.8

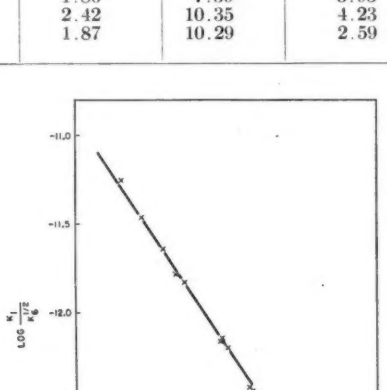

FIG. 1. Arrhenius plot for the reaction of methyl radicals with diethyl ketone.

discussed in a further paper. If the diameters of a methyl radical and a diethyl ketone molecule are assumed to 3.5 and 6.0 Å respectively, a value of 7.4×10^{-4} is obtained for the ratio of the steric factors $P_1/P_6^{\frac{1}{2}}$. Or, assuming $P_6 = 1$, $P_1 = 7.4 \times 10^{-4}$.

(B) The Reaction of Ethyl Radicals with Diethyl Ketone

The reaction mechanism for the photolysis of azoethane in the presence of diethyl ketone is presumably:

$$C_2H_5N_2C_2H_5 + h\nu \rightarrow 2\,C_2H_5 + N_2 \qquad [9]$$

$$2\,C_2H_5 \rightarrow C_4H_{10} \qquad [10]$$

$$2\,C_2H_5 \rightarrow C_2H_4 + C_2H_6 \qquad [11]$$

$$C_2H_5 + C_2H_5N_2C_2H_5 \rightarrow C_2H_6 + C_2H_4N_2C_2H_5 \qquad [12]$$

$$C_2H_5 + C_2H_5COC_2H_5 \rightarrow C_2H_6 + C_2H_4COC_2H_5 \qquad [2]$$

$$C_2H_4N_2C_2H_5 \rightarrow C_2H_4 + N_2 + C_2H_5 \qquad [13]$$

$$C_2H_4COC_2H_5 \rightarrow C_2H_4 + CO + C_2H_5. \qquad [8]$$

Reaction [8] may again be neglected in the temperature range used here. Reaction [13] can also be ignored since it will only slightly affect the kinetics. (For a discussion of the analogous case in the photolysis of diethyl ketone see (5).)

A steady-state treatment of reactions [9] – [12] and [2] gives

$$\frac{k_2}{k_{10}^{\frac{1}{2}}} = \frac{R_{C_2H_6} - R_{C_2H_4}}{R_{C_4H_{10}}^{\frac{1}{2}}[C_2H_5COC_2H_5]} - \frac{k_{12}[C_2H_5N_2C_2H_5]}{k_{10}^{\frac{1}{2}}[C_2H_5COC_2H_5]}$$

The values of $k_{12}/k_{10}^{\frac{1}{2}}$ were taken from the experimental Arrhenius plot for azoethane (2). The results are given in Table II, and in Fig. 2, $\log k_2/k_{10}^{\frac{1}{2}}$ is plotted against $1/T$. From the slope of the curve in Fig. 2 an activation energy of 7.6 kcal. is obtained. If E_{10} is assumed to be zero, the experimental

TABLE II
REACTION OF ETHYL RADICALS WITH DIETHYL KETONE

Temp., °K.	Pressure, cm.		Rate, cc./min. 10^4			$k_2/k_{10}^{\frac{1}{2}} \times 10^{13}$, cm.$^{3/2}$ molecule$^{-\frac{1}{2}}$ sec.$^{-\frac{1}{2}}$
	$C_2H_5N_2C_2H_5$	$C_2H_5COC_2H_5$	C_2H_4	C_2H_6	C_4H_{10}	
322	4.2	2.15	1.225	3.2	8.95	1.79
347	3.6	2.11	1.345	5.21	7.77	3.84
372	3.85	2.05	1.52	7.5	8.78	8.1
397	3.6	2.1	0.627	7.54	3.5	16.2
398	8.1	2.0	1.95	21.6	9.3	14.4
431	3.2	2.3	1.35	18.8	6.3	33.2
431	4.03	2.22	1.64	22.5	7.1	33.2

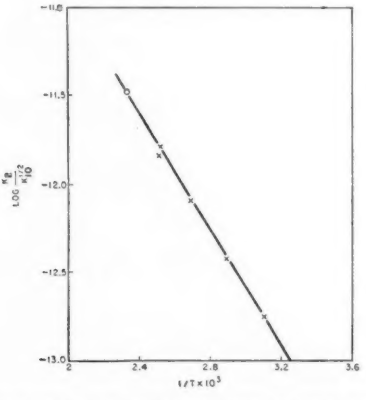

FIG. 2. Arrhenius plot for the reaction of ethyl radicals with diethyl ketone.

value corresponds to E_2. This value is in close agreement with the values found by Kutschke (7.3 kcal.) and Wijnen (7.5 kcal.) in the direct photolysis of diethyl ketone (3). From the experimental value of E_2, the steric factor ratio $P_2/P_{10}^{\frac{1}{2}}$ is calculated to be 7.1×10^{-4}. There is not much direct information about P_{10}, but it is probably not far from unity. Hence $P_2 \approx 7.1 \times 10^{-4}$.

If the results for the two reactions are compared, we have

		E	P
(1)	$CH_3 + C_2H_5COC_2H_5$	7.0 kcal.	7.4×10^{-4}
(2)	$C_2H_5 + C_2H_5COC_2H_5$	7.6 kcal.	7.1×10^{-4}.

The steric factors are thus virtually identical, on the assumption that the recombination of methyl and ethyl radicals both occur with the same efficiency. Since the C–H bond is about 4 kcal. stronger in CH_4 than in C_2H_6, reaction [1] is about 4 kcal. more exothermic than reaction [2]. It would therefore be expected that $E_1 < E_2$. The difference found (0.6 kcal.) is, however, rather smaller than might have been expected.

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DERIVATIVES OF CHLOROBENZENE-2,4-DISULPHONIC ACID[1]

By Marshall Kulka

ABSTRACT

Chlorobenzene-2,4-disulphonates (II), -disulphones (IV), and -disulphonamides (V) have been prepared from chlorobenzene-2,4-disulphonyl chloride (I). The properties and reactions of I–V have been compared with those of related derivatives of *p*-chlorobenzenesulphonic acid and phenoxybenzene-4,4′-disulphonic acid.

Recent investigations have shown that *p*-chlorophenyl (5) and β-chloroethyl *p*-chlorobenzenesulphonates (3) are toxic to insects. In a further search for insecticides, it was decided to prepare for testing derivatives of chlorobenzene-2,4-disulphonic acid. This report of the investigation describes the preparation of II–V from chlorobenzene-2,4-disulphonyl chloride (I) (10); and compares the properties and reactions of I–V with those of related derivatives of *p*-chlorobenzenesulphonic acid (6) and phenoxybenzene-4,4′-disulphonic acid (12). Information regarding the insecticidal activity of these compounds is provided by another communication (8).

Chlorobenzene-2,4-disulphonyl chloride (I) is not affected by chlorine at 160°. This is contrary to the behavior of *p*-chlorobenzenesulphonyl chloride which is converted to *p*-dichlorobenzene under similar conditions (6). The disulphonyl chloride (I) reacts normally with alcohols and phenols to form II when in the presence of sodium hydroxide but only in poor yields or not at all when organic base is used. Thus the reaction products of I, ethylene chlorohydrin, and pyridine were ethylene dichloride and chlorobenzene-2,4-disulphonic acid. Esters of chlorobenzene-2,4-disulphonic acid and allyl alcohol, 1,1,1-trichloro-3-nitro-2-propanol, and 1,1,1-trichloro-2-methyl-2-propanol could not be obtained under any conditions.

Unlike *p*-chlorobenzenesulphinic acid and phenoxybenzene-4,4′-disulphinic acid, chlorobenzene-2,4-disulphinic acid (III) is very soluble in water and liberates sulphur dioxide rapidly when warmed in dilute mineral acid solution. However the sodium salt of III is sufficiently stable to form chlorobenzene-2,4-disulphones (IV) with reactive halogen compounds. *p*-Chlorobenzenesulphinic acid and phenoxybenzene-4,4′-disulphinic acid react readily with aqueous formaldehyde as does *p*-toluenesulphinic acid (2) to form the corresponding hydroxymethyl aryl sulphones but no IV (R = CH_2OH) could be isolated from an aqueous solution of III and formaldehyde. Although *p*-chloro- and *p*-nitrobenzenesulphonyl chlorides undergo the Friedel-Crafts reaction with methoxybenzenes to form diaryl sulphones (1) along with other products, diaryl chlorobenzene-2,4-disulphones (IV, R = aryl) could not be prepared from I and anisole, veratrole, and *m*-dimethoxybenzene using zinc chloride as the condensing agent.

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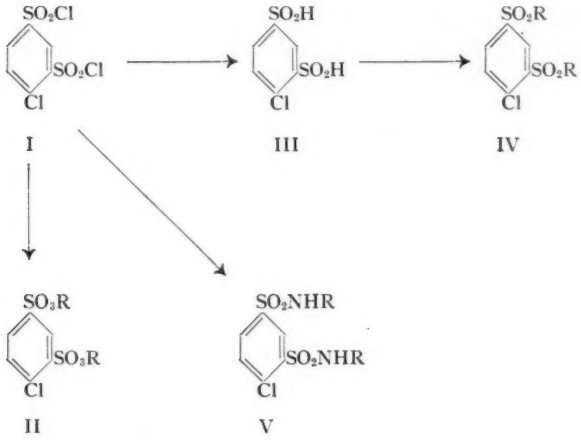

No difficulty was experienced in the preparation of chlorobenzene-2,4-disulphonamides (V) from I and excess amine. It must be cautioned that 1,N,N,N′,N′-pentachlorobenzene-2,4-disulphonamide, which was obtained from chlorobenzene-2,4-disulphonamide (V, R = H) (9) and chlorine, is extremely reactive. A solution of the N,N,N′,N′-tetrachloro-V (R = H) in xylene when warmed on the steam bath resulted in a violent explosion.

Aqueous hydrazine can react with chlorobenzene-2,4-disulphonyl chloride (I) to form either chlorobenzene-2,4-disulphonhydrazide (V, R = NH_2) or the disulphinic acid (III) depending on conditions. When I is treated with excess aqueous hydrazine, V (R = NH_2) precipitates and if this is not filtered it gradually dissolves to form the water soluble III. This shows that the hydrazide must be an intermediate when hydrazine is used in the reduction of an arylsulphonyl halide to the corresponding arylsulphinic acid.

EXPERIMENTAL

1. *Chlorobenzene-2,4-disulphonyl Chloride (I)*

A solution of *p*-chlorobenzenesulphonyl chloride (6) (120 gm.) and chlorosulphonic acid (300 ml.) was heated at 130° for 20 hr. The cooled reaction mixture was cautiously poured onto cracked ice and the precipitated solid extracted with benzene. The benzene extract was quickly washed with cold water, dried, and the solvent distilled off. Crystallization of the residue from carbon tetrachloride yielded 120 gm. (69%) of white solid melting 89–90°; Lit. (10) m.p. 90–91°.

In other experiments the use of a lower reaction temperature resulted in incomplete reaction and the use of less chlorosulphonic acid decreased the yield.

2. *Diethyl Chlorobenzene-2,4-disulphonate (II, R = C_2H_5)*

To a solution of chlorobenzene-2,4-disulphonyl chloride (I) (31 gm.) in benzene (300 ml.) was added absolute ethanol (125 ml.) and pellet sodium

hydroxide (8 gm.) and the reaction mixture stirred at 15–20° for five hours. The resulting mixture was washed with water, the benzene solution dried, and the solvent removed. Crystallization of the residue from ethanol and from benzene – petroleum ether yielded 12 gm. (30%) of white needles melting at 72–73°. Anal. calc. for $C_{10}H_{13}O_6ClS_2$: C, 36.54; H, 3.96. Found: C, 36.52, 36.25; H, 3.85, 4.01.

3. *Dimethyl Chlorobenzene-2,4-disulphonate* (*II*, $R = CH_3$)

This was prepared in 55% yield, using methanol instead of ethanol (see section 2), m.p. 118–119°. Anal. calc. for $C_8H_9O_6ClS_2$: C, 31.96; H, 3.00. Found: C, 32.49, 32.35; H, 3.13, 2.95.

4. *bis*-(2-*Chloroethyl*) *Chlorobenzene-2,4-disulphonate* (*II*, $R = CH_2CH_2Cl$)

A reaction mixture of chlorobenzene-2,4-disulphonyl chloride (I) (30 gm.), ethylene chlorohydrin (80 ml.), and pellet solid hydroxide (8 gm.) was stirred for two hours, the temperature being maintained at 20–30°. Cooling on an ice water bath was essential at the beginning. After it had been allowed to stand overnight, the reaction mixture was extracted with ether, the ether extract washed with water, and the solvent removed. Crystallization of the residue from methanol yielded 30 gm. (75%) of white prisms melting at 72–73°. Anal. calc. for $C_{10}H_{11}O_6Cl_3S_2$: C, 30.20; H, 2.77. Found: C, 30.38, 30.06; H, 2.98, 2.97.

5. *bis*(2-*Chloroethyl*) *Phenoxybenzene-4,4′-disulphonate*

This was prepared in 75% yield from phenoxybenzene-4,4′-disulphonyl chloride (12) and ethylene chlorohydrin (see section 4). It crystallized from benzene–methanol as colorless prisms melting at 82–83°. Anal. calc. for $C_{16}H_{16}O_7Cl_2S_2$: C, 42.20; H, 3.52. Found: C, 42.84, 42.77; H, 3.45, 3.30.

6. *bis*(*p-Chlorophenyl*) *Chlorobenzene-2,4-disulphonate* (*II* $R = p\text{-}ClC_6H_4$)

To a solution of *p*-chlorophenol (35 gm.), sodium hydroxide (9 gm.), and water (35 ml.) was added a solution of chlorobenzene-2,4-disulphonyl chloride (I) (30 gm.) in benzene (300 ml.) and the reaction mixture was stirred for five hours. The temperature was maintained at 25–35° by occasional cooling. The benzene solution was separated, washed with aqueous sodium hydroxide and water, and then concentrated to about 50 ml. On cooling there crystallized 43 gm. (92%) of white prisms which on recrystallization from benzene–methanol melted at 141–142°. Anal. calc. for $C_{18}H_{11}O_6Cl_3S$: C, 43.78; H, 2.23. Found: C, 43.77; H, 2.23.

7. *bis*(*p-Nitrophenyl*) *Chlorobenzene-2,4-disulphonate* (*II*, $R = p\text{-}NO_2C_6H_4$)

This compound was prepared in 75% yield from *p*-nitrophenol and I (see section 6). (Reaction time 18 hr.) The white prisms melted at 147–148° after crystallization from benzene. Anal. calc. for $C_{18}H_{11}N_2O_{10}ClS_2$: C, 42.00; H, 2.14. Found: C, 42.24, 42.08; H, 2.28, 2.45.

8. *bis*(8-*Quinolyl*) *Chlorobenzene-2,4-disulphonate* (*II*, $R = C_9H_6N$)

This was prepared in 82% yield from 8-hydroxyquinoline and I (see section 6). The light-tan prisms melted at 174–175° after crystallization from acetone.

Anal. calc. for $C_{24}H_{15}N_2O_6ClS_2$: C, 54.70; H, 2.85. Found: C, 54.26, 54.80; H, 2.84, 2.84.

9. *bis(p-Chlorophenyl) Phenoxybenzene-4,4′-disulphonate*

This was prepared in 80% yield from phenoxybenzene-4,4′-disulphonyl chloride (12) and *p*-chlorophenol (see section 6). It crystallized from methanol as colorless prisms and melted at 104–105°. Anal. calc. for $C_{24}H_{16}O_7Cl_2S_2$: C, 52.26; H, 2.90. Found: C, 52.34, 52.63; H, 2.74, 2.55.

10. *8-Quinolyl p-Chlorobenzenesulphonate*

This was prepared in 70% yield, from *p*-chlorobenzenesulphonyl chloride and 8-hydroxyquinoline (see section 6). The light-tan needles melted at 120–121° after crystallization from methanol. Anal. calc. for $C_{15}H_{10}NO_3ClS$: C, 56.34; H, 3.13. Found: C, 56.23; 56.18; H, 3.03, 3.14.

11. *Chlorobenzene-2,4-disulphinic Acid (III)*

To a stirred solution of sodium sulphite (175 gm.) in water (500 ml.) was added chlorobenzene-2,4-disulphonyl chloride (I) (50 gm.) and benzene (50 ml.) and the reaction mixture was stirred at 50–60° for five hours. The reaction mixture was allowed to stand overnight, and then was treated with concentrated hydrochloric acid with cooling at 15–20° and the sulphur dioxide was removed *in vacuo* at room temperature. The resulting solution was extracted with five 500-ml. portions of ether and the solvent removed from the extract. The residual oil which was unstable in the presence of warm hydrochloric acid would not crystallize. It was used directly for the preparation of the sulphones (see below).

12. *Dimethyl Chlorobenzene-2,4-disulphone (IV, R = CH_3)*

A solution of crude chlorobenzene-2,4-disulphinic acid (III) (15 gm.), water (100 ml.), and chloroacetic acid (15 gm.) was treated with sodium carbonate until just alkaline. The resulting solution was heated on the steam bath for two days. The precipitated sulphone (11 gm. or 70%) was filtered, washed, and crystallized from ethanol. The white needles melted at 174–175°. Anal. calc. for $C_8H_9O_4ClS_2$: C, 35.76; H, 3.35. Found: C, 35.79, 35.93; H, 3.47, 3.40.

13. *bis(Chloromethyl) Chlorobenzene-2,4-disulphone (IV, R = CH_2Cl)*

This was prepared in 25% yield from dichloroacetic acid and III (see section 12). The white solid melted at 137–138° after crystallization from methanol. Anal. calc. for $C_8H_7O_4Cl_3S_2$: C, 28.45; H, 2.07; Cl, 31.56. Found: C, 28.30; H, 1.99; Cl, 31.20.

14. *bis(Chloromethyl) Phenoxybenzene-4,4′-disulphone*

This was prepared in 50% yield from phenoxybenzene-4,4′-disulphinic acid and dichloroacetic acid (see section 12). It crystallized from methanol as white needles melting at 139–140°. Anal. calc. for $C_{14}H_{12}O_5Cl_2S_2$: C, 42.53; H, 3.04. Found: C, 42.83; H, 2.80.

15. *Dimethyl Phenoxybenzene-4,4′-disulphone*

This was prepared in 75% yield from phenoxybenzene-4,4′-disulphinic acid and chloroacetic acid (see section 12). It crystallized from methanol as white prisms melting at 182–183°. Anal. calc. for $C_{14}H_{14}O_5S_2$: C, 51.53; H, 4.29. Found: C, 52.06, 51.82; H, 3.96, 4.16.

16. *Hydroxymethyl p-Chlorophenylsulphone*

Following the method of von Meyer (7) for the preparation of hydroxymethyl *p*-tolylsulphone, *p*-chlorobenzenesulphinic acid (50 gm.) and 40% formaldehyde (100 ml.) were stirred for one hour. The white solid (52 gm. or 90%) was filtered, washed, dried, and crystallized from benzene, m.p. 111–112°. Anal. calc. for $C_7H_7O_3ClS$: C, 40.67; H, 3.39. Found: C, 40.93, 40.66; H, 3.27, 3.36. Heating this compound with phenyl isocyanate did not yield the urethane.

17. *bis(Hydroxymethyl) Phenoxybenzene-4,4′-disulphone*

This was prepared in 90% yield from phenoxybenzene-4,4′-disulphinic acid (prepared in a manner similar to that of III in section 11) and formaldehyde (see section 16). It crystallized from dilute formaldehyde as a white solid melting at 151–153° (with decomposition). Anal. calc. for $C_{14}H_{14}O_7S_2$: C, 46.92; H, 3.91. Found: C, 47.05, 47.02; H, 3.95, 4.14.

18. *p-Chlorophenyl 3,4-Dimethoxyphenylsulphone*

The method of Burton and Hoggarth (1) was employed. A reaction mixture of *p*-chlorobenzenesulphonyl chloride (40 gm.), veratrole (40 gm.), and zinc chloride (30 gm.) was stirred in an open beaker and heated at 120–130° for 15 min. Hydrogen chloride was evolved with considerable frothing. The cooled reaction mixture was treated with dilute hydrochloric acid and then extracted with benzene. The benzene solution was washed with dilute hydrochloric acid, with aqueous alkali, and with water and the solvent was removed. The residue was fractionally distilled yielding essentially two fractions, one boiling at 170–180° (0.2 mm.) and the other at 180–200° (0.2 mm.). The first fraction was crystallized from ethanol to yield white needles (16 gm. or 28%) melting at 99–100° alone or in admixture with *o-methoxyphenyl p-chlorobenzenesulphonate* (see section 19). This is apparently formed through demethylation of veratrole and reaction of the resulting guaiacol with *p*-chlorobenzenesulphonyl chloride.

The second fraction which consisted mainly of *p-chlorophenyl 3,4-dimethoxyphenylsulphone* was boiled for three hours with aqueous–alcoholic alkali to free it from *o*-methoxyphenyl *p*-chlorobenzenesulphonate. The alcohol was removed and the precipitate crystallized from ethanol. The white needles (4 gm. or 7%) melted at 140–141°. Anal. calc. for $C_{14}H_{13}O_4ClS$: C, 53.75; H, 4.16. Found: C, 54.17, 54.21; H, 4.33, 4.12.

19. *o-Methoxylphenyl p-Chlorobenzenesulphonate*

This was prepared in 70% yield from *p*-chlorobenzenesulphonyl chloride and guaiacol (see section 6). The white needles melted at 99–100° after

crystallization from ethanol. Anal. calc. for $C_{13}H_{11}O_4ClS$: C, 52.26; H, 3.68; OCH_3, 10.39. Found: C, 52.66, 52.46; H, 3.67, 3.77; OCH_3, 10.37, 10.53.

20. *p-Chlorophenyl p-Methoxyphenylsulphone*

This was prepared in 15% yield from *p*-chlorobenzenesulphonyl chloride and anisole (see section 18). The white prisms melted at 70–71° after crystallization from methanol. Anal. calc. for $C_{13}H_{11}O_3ClS$: C, 55.22; H, 3.89. Found: C, 55.41, 55.20; H, 3.58, 4.16.

21. *p,p'-Dichlorobenzhydryl p-Chlorophenylsulphone*

The method of Hinsberg (4) was employed. A solution of *p,p'*-dichlorobenzhydrol (11) (5 gm.), *p*-chlorobenzenesulphinic acid (5 gm.), acetic acid (25 ml.), and two drops of concentrated hydrochloric acid were heated under reflux for four hours. The cooled reaction mixture was poured into water, extracted with ether, the ether extract washed with dilute aqueous sodium hydroxide and with water, and the solvent removed. The residue crystallized from benzene–methanol as white needles (6.1 gm.) which melted at 105–106°. Anal. calc. for $C_{19}H_{13}O_2Cl_3S$: C, 55.41; H, 3.16. Found: C, 55.56; H, 3.24.

22. *1,N,N,N',N'-Pentachlorobenzene-2,4-disulphonamide*

To a stirred solution of chlorobenzene-2,4-disulphonamide (9) (15 gm.) in sodium hydroxide (6 gm.) and water (250 ml.) was added chloroform (300 ml.) and then excess chlorine was passed in for one hour. The temperature was maintained at 25–30° by occasional cooling. The chloroform layer was separated, washed with water, concentrated to about 30 ml., and allowed to cool. White crystals (16 gm. or 64%) separated which melted at 148–149°. Anal. calc. for $C_6H_3N_2O_4Cl_5S_2$: C, 17.62; H, 0.73. Found: C, 18.01, 18.22; H, 0.94, 1.06.

This compound is a dangerous chlorinating agent. When equimolecular quantities of it and *p*-xylene were mixed and heated on the steam bath a violent explosion resulted.

23. *N,N,N',N'-Tetramethyl-1-chlorobenzene-2,4-disulphonamide*

Chlorobenzene-2,4-disulphonyl chloride (20 gm.) and 40% aqueous dimethylamine (100 ml.) were heated on the steam bath and stirred for two hours. The white precipitate was filtered, washed, and crystallized twice from methanol, m.p. 132–133°; yield, 19 gm. or 60%. Anal. calc. for $C_{10}H_{15}N_2O_4ClS_2$: C, 36.75; H, 4.60. Found: C, 37.16; H, 4.69.

24. *N,N'-Di-2-pyridyl-1-chlorobenzene-2,4-disulphonamide* (*V*, *R* = *2-pyridyl*)

To a solution of 2-aminopyridine (35 gm.) in benzene (75 ml.) was added a solution of chlorobenzene-2,4-disulphonyl chloride (25 gm.) in benzene (100 ml.). The resulting reaction mixture was heated under reflux for one-half hour and then poured into cold water. The yellow precipitate was filtered and washed with dilute hydrochloric acid, water, benzene, and acetone. It was then redissolved in dilute aqueous potassium hydroxide, the solution filtered, and the filtrate was acidified with acetic acid. The precipitate (27 gm.

or 80%) was filtered, washed, and dried, m.p. 280° (with decomposition). Anal. calc. for $C_{16}H_{13}N_4O_4ClS_2$: C, 45.21; H, 3.06. Found: C, 44.92, 45.02; H, 3.59, 3.36.

25. *N-2-Pyridyl-p-chlorobenzenesulphonamide*

This was prepared in 80% yield from 2-aminopyridine and *p*-chlorobenzenesulphonyl chloride (see section 24). It crystallized from methanol in the form of white needles which melted at 193–194°. Anal. calc. for $C_{11}H_9N_2O_2ClS$: C, 49.17; H, 3.35. Found: C, 49.21, 49.56; H, 3.29, 3.37.

26. *N,N'-bis(2-Hydroxyethyl)-1-chlorobenzene-2,4-disulphonamide* (*V*, $R = CH_2CH_2OH$)

This was prepared in 35% yield from chlorobenzene-2,4-disulphonyl chloride and ethanolamine using chloroform as solvent instead of benzene (see section 24). It crystallized from benzene–methanol as white needles melting at 127–128°. Anal. calc. for $C_{10}H_{15}N_2O_6ClS$: C, 33.48; H, 4.18. Found: C, 33.70, 33.86; H, 4.12, 4.11.

27. *Chlorobenzene-2,4-disulphonyl-N,N'-bis(1,2,3,4-tetrahydroquinoline)*

This was prepared in 54% yield from 1,2,3,4,-tetrahydroquinoline and chlorobenzene-2,4-disulphonyl chloride (see section 24). It crystallized from benzene as pink prisms melting at 116–117°. Anal. calc. for $C_{24}H_{23}N_2O_4ClS_2$: C, 57.32; H, 4.58. Found: C, 57.34, 57.48; H, 4.48, 4.41.

28. *N-(p-Chlorophenylsulphonyl)-1,2,3,4-tetrahydroquinoline*

This was prepared in 60% yield from 1,2,3,4-tetrahydroquinoline and *p*-chlorobenzenesulphonyl chloride (see section 24). It crystallized from methanol as white needles melting at 94–95°. Anal. calc. for $C_{15}H_{14}NO_2ClS$: C, 58.55; H, 4.55; N, 4.55. Found: C, 58.13, 58.43; H, 4.30, 4.46; N, 4.91, 4.70.

29. *Chlorobenzene-2,4-disulphonyl bis-Hydrazide* (*V*, $R = NH_2$)

To a stirred cold solution of chlorobenzene-2,4-disulphonyl chloride (20 gm.) in benzene (70 ml.) was added a chilled solution of 85% hydrazine hydrate (20 ml.) in water (20 ml.). The reaction mixture was stirred and cooled at 10° for not more than two hours. (Further reaction occurs to form chlorobenzene-2,4-disulphinic acid if more time is allowed.) The white precipitate (16 gm. or 80%) was filtered, washed, dried, and crystallized quickly from pyridine–ether, m.p. 133° (with decomposition). Anal. calc. for $C_6H_9N_4O_4ClS_2$: C, 23.96; H, 3.00. Found: C, 23.90; H, 2.79.

This compound is insoluble in benzene, methanol, ether, and cold water. It is soluble in hot water but decomposition occurs on prolonged heating.

In another experiment twice the amount of hydrazine hydrate was used and the reaction mixture was allowed to stand overnight. The chlorobenzene-2,4-disulphonyl bis-hydrazide, which first precipitated, gradually dissolved. The aqueous solution was separated, acidified with 50% sulphuric acid, the precipitated hydrazine sulphate was filtered, and the filtrate extracted exhaustively with ether. Removal of the ether left the oily chlorobenzene-2,4-disulphinic acid (8 gm.). This, when treated with chloroacetic acid (see

section 12), yielded a sulphone which did not depress the melting point of dimethyl chlorobenzene-2,4-disulphone (IV, R = CH_3).

30. *p-Chlorophenylsulphonhydrazide*

This was prepared in 92% yield from *p*-chlorobenzenesulphonyl chloride and hydrazine (see section 29). It crystallized from benzene as white woolly needles melting at 117–118° (with decomposition). Anal. calc. for $C_6H_7N_2O_2ClS$: C, 34.85; H, 3.39; N, 13.56. Found: C, 35.30, 34.72; H, 3.36, 3.74; N, 13.63.

In another experiment where the reaction was carried out at steam bath temperature, a 70% yield of *p*-chlorobenzenesulphinic acid was obtained.

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DIHYDRO-N-*nor*GELSEMINE AND SOME OF ITS DERIVATIVES[1]

By Thelma Habgood and Léo Marion

ABSTRACT

Treatment of gelsemine with cyanogen bromide produced N-cyano-*nor*gelsemine which on catalytic hydrogenation gave rise to N-cyanodihydro-N-*nor*gelsemine, identical with the product of the reaction of cyanogen bromide with dihydrogelsemine. N-Cyanodihydro-N-*nor*gelsemine was hydrolyzed with hydrochloric acid to dihydro-N-*nor*gelsemine which readily formed a mono- or a dibenzoyl derivative according to the conditions, and a *p*-toluenesulphonamide. The action of phosphorus pentachloride on the monobenzoyl derivative gave rise to N-benzoylchlorodihydro-N-*nor*gelsemine, hydrolyzable by hydrochloric acid to chlorodihydro-N-*nor*gelsemine. This chloro compound was converted by the action of formaldehyde and formic acid to chlorodihydrogelsemine, identical with the product of the action of phosphorus pentachloride on dihydrogelsemine. Chlorination of dihydrogelsemine with chlorine produced dichlorogelsemine.

It has now been well established that gelsemine is a 3,3-disubstituted oxindole (4,8) but little is known about the structure of the second moiety of the molecule. The basic N(b) carries a methyl group, and there are present a readily reducible double bond which has been claimed to involve an exocyclic methylene group (3,4), and an ether ring. Since gelsemine contains six rings, the unknown moiety must include four of these. The usual conditions of the Hofmann degradation reconvert the metho-base to the original alkaloid, while distillation of the metho-base *in vacuo* does not cause the opening of the ring containing N(b) as first assumed (5) but brings about a transmethylation giving rise to N(a)-methylgelsemine (6,9). It was thought that cyanogen bromide might react with N(b) and thus afford a means of degrading that part of the molecule in which it is contained. Before this work had reached completion, Jones and Stevens (7) reported their investigation of this reaction. We have succeeded, however, in preparing N-benzoyldihydro-N-*nor*gelsemine and shown that phosphorus pentachloride chlorinates the benzene ring present in the alkakoid instead of cleaving the N(b)-containing ring. Furthermore, a number of well defined crystalline derivatives have been obtained which are deemed worth recording.

According to Forsyth *et al.* (2) the action of cyanogen bromide on gelsemine gives rise to a substance yielding imperfectly concordant results which they assumed to be a mixture. In our hands this reaction yielded N-cyano-N-*nor*gelsemine, $C_{20}H_{19}O_2N_3$, which could be hydrogenated catalytically to N-cyanodihydro-N-*nor*gelsemine, $C_{20}H_{21}O_2N_3$, identical with the product obtained directly by the action of cyanogen bromide on dihydrogelsemine. N-Cyanodihydro-N-*nor*gelsemine was first reported by Jones and Stevens (7). On hydrolysis with hydrochloric acid it produced crystalline dihydro-N-*nor*gelsemine, $C_{19}H_{22}O_2N_2$, which formed both a picrate and a perchlorate. Dihydro-N-*nor*gelsemine gave rise to a *p*-toluenesulphonyl derivative and, in

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the Schotten-Baumann reaction, to a monobenzoyl derivative, while it gave a dibenzoyl derivative when treated with benzoyl chloride and pyridine. An attempt to degrade monobenzoyldihydro-*nor*gelsemine with phosphorus pentachloride resulted in the formation of benzoylchlorodihydro-*nor*gelsemine which on hydrolysis with hydrochloric acid produced crystalline chlorodihydro-*nor*gelsemine. This chloro compound could not be recrystallized without some decomposition, although it formed a stable perchlorate and a *p*-toluenesulphonamide.

Chlorine could not be removed from chlorodihydro-*nor*gelsemine either by treatment with chromous chloride or with zinc and acetic acid, both of which reagents left the material unchanged. Catalytic hydrogenation seemed to effect partial dehalogenation only as indicated by examination of the various fractions isolated by chromatography of the product (see experimental). The firmness with which the chlorine is retained makes it likely that it is located in the benzene ring of the alkaloid. At any rate, the infrared spectra of the various compounds (Table I) seem to support this possibility.

TABLE I

INFRARED ABSORPTION OF GELSEMINE DERIVATIVES ATTRIBUTABLE TO SUBSTITUTED BENZENE RING*

Compound	Absorption bands (in wave numbers)					
Gelsemine		742	756			
Dihydrogelsemine	720	740,745	760			
Cyano-*nor*gelsemine		745	750,757			
Cyanodihydro-*nor*gelsemine		743	756			
Dihydro-*nor*gelsemine	738	747	760			
Bz-chlorodihydro-*nor*gelsemine	704			824		
Chlorodihydro-*nor*gelsemine	720			808,818		
Chloro-*p*-toluenesulphonamide	707	748†		815		
Chlorodihydrogelsemine				810		
Dichlorodihydrogelsemine	732	750,769				859

**The infrared spectra were determined on nujol mulls with a Perkin–Elmer double beam spectrometer, model 21.*

†*Weak band.*

Chlorodihydro-N-*nor*gelsemine was converted by heating with formaldehyde and formic acid to chlorodihydrogelsemine identical with the product obtainable by treatment of dihydrogelsemine with phosphorus pentachloride. Chlorination of dihydrogelsemine with chlorine in chloroform solution gave rise to dichlorodihydrogelsemine, $C_{20}H_{22}O_2N_2Cl_2$.

A comparison of the infrared spectra (Table I) of gelsemine, dihydrogelsemine, cyano-N-*nor*gelsemine, and cyanodihydro-N-*nor*gelsemine with those of benzoylchlorodihydro-N-*nor*gelsemine, chlorodihydro-N-*nor*gelsemine, its *p*-toluenesulphonamide, and of chlorodihydrogelsemine shows that the band at 756 – 760 cm.$^{-1}$ present in the first four and attributable to a disubstituted benzene ring (1) is absent in the spectra of the chloro compounds which all contain a new band at 815 – 824 cm.$^{-1}$ attributable to a trisubstituted benzene ring (1). It is, therefore, very probable that the chlorine has entered the benzene ring of the alkaloid. The infrared spectrum of dichlorodihydrogelsemine

contains a band at 859 cm.$^{-1}$ instead of the absorption at 815 – 824 cm.$^{-1}$ so that the substance probably contains both chlorine atoms in the benzene ring.

The ultraviolet spectra of the gelsemine derivatives described show that the introduction of chlorine into the molecule causes a shift of the spectrum in the direction that would be expected from the addition of such an auxochrome to the chromophoric group.

EXPERIMENTAL[2]

N-Cyano-N-nor*gelsemine*

A solution of gelsemine containing acetone of crystallization (1.041 gm.) in dry chloroform (20 ml.) was refluxed for six hours with freshly distilled cyanogen bromide (1.5 gm.). The reaction mixture was evaporated to dryness under reduced pressure and the residue taken up in *ca.* 25 ml. of chloroform and filtered. The chloroform insoluble material (359 mgm.) consisted of crude gelsemine hydrobromide, m.p. 315–322°. The chloroform solution, washed with dilute sodium hydroxide solution and evaporated to dryness under reduced pressure, gave 678 mgm. of pale yellow foam which crystallized on the addition of a few drops of methanol, m.p. 217.5 – 219°. Chromatography on alumina from benzene solution and elution with benzene–chloroform mixtures yielded a product which after recrystallization from methanol consisted of colorless prisms, m.p. 217.5–218°. A substance which was probably slightly impure N-cyano-N-*nor*gelsemine is reported in the literature as melting at 216° (2). Calc. for $C_{20}H_{19}O_2N_3$: C, 72.05; H, 5.74; N, 12.61. Found: C, 72.01; H, 5.81; N, 12.70; N·CH_3, 1.28, 1.36%[3].

N-Cyanodihydro-N-nor*gelsemine*

(*a*) *By Hydrogenation of N-Cyano-N*-nor*gelsemine*

Cyano-*nor*gelsemine (197 mgm.) dissolved in methanol (15 ml.) was hydrogenated at low pressure in the presence of platinum oxide (45 mgm.). Two-thirds of the calculated volume of hydrogen was absorbed. Chromatography of the product from benzene solution with chloroform elution gave 161 mgm. of colorless foam which was dissolved in hot methanol. On cooling the solution deposited colorless prisms (75 mgm.), m.p. 258–262°. After three recrystallizations from methanol, m.p. 269–270.5° (reported m.p. 269° (7)). Calc. for $C_{20}H_{21}O_2N_3$: C, 71.62; H, 6.31; N, 12.53. Found: C, 71.50, 71.55, 71.68; H, 6.30, 6.19, 6.74; N, 12.19, 12.37%.

(*b*) *From Dihydrogelsemine*

A solution of dihydrogelsemine (4.030 gm.) in dry benzene (75 ml.) to which was added freshly distilled cyanogen bromide (6 gm.) was refluxed for 16 hr. The reaction mixture, worked up as in the preparation of cyano-*nor*gelsemine,

[2]*All melting points are corrected.*

[3]*The theoretical value for one N-CH_3 is about 4.3%. N-Cyano-N-*nor*gelsemine contains no imino methyl, and the small value obtained may be due to some reduction of the cyano group. At any rate the infrared spectra of the* nor*gelsemine derivatives contain only a weak band at 1375 cm.$^{-1}$ and no absorption at 2750 cm.$^{-1}$, whereas the spectra of gelsemine and dihydrogelsemine show in both these regions definite absorption attributable to an N-CH_3 group.*

yielded a pale yellow oil (3.819 gm.) which crystallized from methanol (first crop, 2.340 gm.), m.p. 268.5–271° either alone or in admixture with N-cyanodihydro-N-*nor*gelsemine obtained by procedure (*a*).

*Dihydro-N-*nor*gelsemine*

N-Cyanodihydro-N-*nor*gelsemine (4.086 gm.) was hydrolyzed by refluxing with ethanol (75 ml.) and concentrated hydrochloric acid (30 ml.) for 96 hr. The clear yellow solution was concentrated to a small volume, diluted with water, and extracted with ether to remove any nonbasic material. The extracted aqueous solution was alkalized with dilute aqueous potassium hydroxide. This caused the precipitation of a white powder which was filtered and dried (3.726 gm.). A portion of this base (265 mgm.) was crystallized from methanol from which it separated as colorless prisms (103 mgm.), m.p. 299.5–302° and after one further crystallization, m.p. 301.5–302.5°. Calc. for $C_{19}H_{22}O_2N_2$: C, 73.52; H, 7.14; N, 9.03. Found: C, 73.79; H, 7.44; N, 8.92%.

The base formed a picrate which separated from ethanol as yellow prisms, m.p. 275–276°(dec.). The melting point reported in the literature is 281–282° (7).

Dihydro-N-*nor*gelsemine also formed a perchlorate which, twice recrystallized from water, consisted of colorless prisms, m.p. 295.5° (dec.). Calc. for $C_{19}H_{22}O_2N_2HClO_4$: C, 55.52; H, 5.65; N, 6.84. Found: C, 54.89, 54.73; H, 6.09, 6.18; N, 6.50%. (The salt invariably exploded during the initial stages of the analysis, and this may account for the low figures obtained.)

*N-p-Toluenesulphonyldihydro-N-*nor*gelsemine*

The uncrystallized base (365 mgm.) dissolved in pyridine (5 ml.) was allowed to stand for 24 hr. with *p*-toluenesulphonyl chloride (410 mgm.). The solvent was then distilled under reduced pressure, the residue dissolved in chloroform, and the solution washed with dilute hydrochloric acid. After evaporation of the chloroform a residue was obtained which was dissolved in benzene and chromatographed on alumina. Elution with benzene gave a small first fraction consisting of a pale yellow oil which was likely *p*-toluenesulphonyl chloride and a main fraction. After evaporation of the solvent the main fraction was a colorless foam (332 mgm.) which crystallized on the addition of methanol, m.p. 209.5 – 212°. Two further recrystallizations from methanol raised the melting point, 214–214.5°. Calc. for $C_{26}H_{28}O_4N_2S$: C, 67.15; H, 6.07; N, 6.02. Found: C, 67.57; H, 6.18; N, 6.10%.

*Benzoylation of Dihydro-*nor*gelsemine*

(*a*) A solution of dihydro-*nor*gelsemine (1.145 gm.) in chloroform (30 ml.) and dioxane (5 ml.) was shaken with 5% aqueous potassium hydroxide (5 ml.) and benzoyl chloride (0.5 ml.). The addition of alkali and benzoyl chloride in the same quantities was repeated twice at 15 min. intervals. When the odor of benzoyl chloride had disappeared, the chloroform layer was washed with dilute sulphuric acid, dried, and evaporated. It left a colorless foam which on addition of methanol gave crystalline N-monobenzoyldihydro-N-*nor*gelsemine, m.p. 268–274° (1.344 gm.).

(*b*) To a solution of dihydro-*nor*gelsemine (615 mgm.) in pyridine (7 ml.) was added benzoyl chloride (1 ml.). After two hours at room temperature, the solution was refluxed for 15 min. and subsequently evaporated to dryness under reduced pressure. The residue was dissolved in chloroform, washed first with dilute potassium hydroxide solution and then with dilute sulphuric acid. After evaporation of the chloroform the residual oil was dissolved in benzene and chromatographed on alumina. Elution with benzene and methylene chloride gave 727 mgm. of colorless foam which crystallized from methanol as colorless prisms, m.p. 227.5 – 228.5°. One further recrystallization gave dibenzoyldihydro-*nor*gelsemine, m.p. 229–229.5°. Calc. for $C_{32}H_{36}O_4N_2$: C, 75.87; H, 5.97; N, 5.53. Found: C, 75.61; H, 6.15; N, 5.53%.

Further elution with chloroform brought down 224 mgm. of a pale yellow foam which crystallized from methanol, m.p. 274 – 276°, identical with monobenzoyldihydro-*nor*gelsemine prepared by the Schotten-Baumann reaction. Two further recrystallizations from methanol raised the melting point to 279–280°. Calc. for $C_{26}H_{26}O_3N_2$: C, 75.34; H, 6.32; N, 6.76, Found: C, 75.61; H, 6.73; N, 6.65%.

*Attempted Degradation of Benzoyldihydro-*norgelsemine *With Phosphorus Pentachloride*

A mixture of monobenzoyldihydro-*nor*gelsemine (301 mgm.), freshly sublimed phosphorus pentachloride (718 mgm.) and dioxane (10 ml.) was refluxed for eight hours. After the addition of a few drops of water, the solvent was removed under reduced pressure, the residual gum dissolved in chloroform, and the solution washed first with dilute hydrochloric acid and afterwards with dilute ammonia. Evaporation of the chloroform left a pale yellow foam (272 mgm.) which crystallized from methanol as colorless prisms, m.p. 297–302°. Three recrystallizations from methanol gave pure benzoylchlorodihydro-*nor*gelsemine, m.p. 312.5 – 313.5°. Calc. for $C_{26}H_{27}O_3N_2Cl$: C, 69.24; H, 6.04; N, 6.21. Found: C, 70.78, 70.25; H, 6.16, 5.73; N, 6.53, 6.23%.

*Chlorodihydro-N-*norgelsemine

Benzoylchlorodihydro-*nor*gelsemine (68 mgm.) was dissolved in ethanol (10 ml.) and concentrated hydrochloric acid (5 ml.). The solution was refluxed for 16 hr. and evaporated to dryness under reduced pressure. The residue was dissolved in water and the solution extracted with chloroform and then alkalized with sodium hydroxide. The precipitated base was collected by extraction with chloroform. Evaporation of this chloroform extract left a foam which crystallized from acetone as colorless needles, m.p. 244 – 248°. Further crystallization lowered the melting point to 240 – 243° and caused the appearance of a yellow color in the mother liquor. The perchlorate of this base separated from methanol as colorless needles, m.p. > 340°. Calc. for $C_{19}H_{21}O_2N_2Cl.HClO_4$: C, 51.25; H, 4.98; N, 6.29. Found: C, 51.50; H, 5.07; N, 6.46%. The base also yielded a *p*-toluenesulphonamide prepared as described for that of dihydro-*nor*gelsemine. It was chromatographed in benzene solution on alumina and eluted with ether. The eluate yielded the product which after two crystallizations from methanol consisted of elongated prisms which

on slow heating gave off solvent at 130°, resolidified and melted at 204–204.5°. Calc. for $C_{26}H_{27}O_4N_2SCl$: C, 62.58; H, 5.46; N, 5.62. Found: C, 62.81; H, 5.88; N, 5.62%.

*Attempted Reduction of Chlorodihydro-N-*nor*gelsemine*

(*a*) *With Chromous Chloride*

A solution of chlorodihydro-N-*nor*gelsemine (350 mgm.) in absolute ethanol (10 ml.) was refluxed under nitrogen for three hours with an ethanolic solution of chromous chloride prepared from chromic chloride hexahydrate (4 gm.), amalgamated zinc (3 gm.), and concentrated hydrochloric acid (5 ml.). The reaction mixture was concentrated under reduced pressure, diluted with water (50 ml.), alkalized with ammonia, and extracted with three portions of ether. The combined dried extract when evaporated to dryness left a residual powder (271 mgm.) which was dissolved in benzene–chloroform (1:1) and chromatographed on alumina. Elution with chloroform containing 5% of methanol brought down the product which on evaporation of the solvent consisted of a pale yellow foam (269 mgm.). This only partially crystallized on addition of a few drops of methanol (m.p. 196–219°). The solid impure base was therefore benzoylated under Schotten-Baumann conditions and the product crystallized from methanol, m.p. 310–313.5°, either alone or in admixture with benzoyl-chlorodihydro-N-*nor*gelsemine.

(*b*) *By Catalytic Hydrogenation*

Chlorodihydro-*nor*gelsemine (288 mgm.) dissolved in methanol was hydrogenated at low pressure in the presence of platinum oxide (29 mgm.). In two hours 80% of the calculated volume of hydrogen was absorbed. The solution was filtered to remove the catalyst and evaporated to dryness. It left a residue which was dissolved in chloroform and the solution after washing with dilute aqueous potassium hydroxide was evaporated to dryness. The residual colorless foam was dissolved in benzene and chromatographed on alumina. Elution with benzene containing increasing concentrations of ether, then with chloroform, failed to give well defined fractions. The fractions eluted with benzene containing 10% of ether gave material which crystallized partially on addition of a few drops of methanol. This material still contained chlorine and its infrared absorption spectrum still contained a band at 810 $cm.^{-1}$ indicative of an unsymmetrically trisubstituted phenyl ring. The fractions eluted with benzene containing 50% of ether yielded material containing a mere trace of halogen and had infrared absorption spectra no longer showing absorption at 810 $cm.^{-1}$, but containing two bands at 740 and 760 $cm.^{-1}$ characteristic of the *o*-disubstituted benzene ring.

(*c*) *With Zinc and Acetic Acid*

Chlorodihydro-*nor*gelsemine (213 mgm.) was refluxed with granular zinc (1.5 gm.) and glacial acetic acid (8 ml.) for three hours. The reaction mixture was diluted with water and the liquor decanted from the zinc which was washed by decantation. The combined decantate was alkalized with concentrated aqueous potassium hydroxide and extracted with chloroform. Evaporation

of the chloroform extract left a white solid (197 mgm., m.p. 204.5–211°) which was converted to the *p*-toluenesulphonamide by the method already described. Chromatography on alumina in benzene solution and elution with ether yielded a product (217 mgm.) which after crystallization from methanol consisted of colorless prisms which lost solvent at 130° and melted at 202–203.5°, either alone or in admixture with N-*p*-toluenesulphonylchlorodihydro-N-*nor*gelsemine.

Chlorodihydrogelsemine

(*a*) *By Methylation of Chlorodihydro-N-*norgelsemine

A mixture of chlorodihydro-N-*nor*gelsemine (408 mgm.), 90% formic acid (3 ml.) and 37% formaldehyde solution (3 ml.) was heated on the steam bath under reflux for six hours, then allowed to stand overnight, and heated again for 30 min. after the addition of concentrated hydrochloric acid. The reaction mixture was evaporated to dryness under reduced pressure and the residue taken up in water (50 ml.). The solution was filtered to remove some insoluble material and washed with ether. The aqueous solution was alkalized with aqueous potassium hydroxide and extracted with chloroform. Evaporation of the chloroform extract left a yellow foam (366 mgm.) which was dissolved in benzene containing 5% of chloroform and chromatographed on alumina. Elution with benzene containing 2% methanol gave a substance (184 mgm.) which was rechromatographed in methylene dichloride solution on the same adsorbent. Elution with methylene dichloride yielded the compound (47 mgm.) which crystallized from acetone as colorless plates, m.p. 218.5 – 221.5°. Calc. for $C_{20}H_{23}O_2N_2Cl$: N, 7.81; N·CH_3, 4.19. Found: N, 7.96; N·CH_3, 3.82%. The base could not be benzoylated under Schotten-Baumann conditions.

(*b*) *By Chlorination of Dihydrogelsemine*

To a solution of dihydrogelsemine (677 mgm.) in dioxane (25 ml.), phosphorus pentachloride (2.34 gm.) was added and the mixture refluxed for six hours. The reaction mixture was concentrated under reduced pressure, diluted with water, alkalized with dilute aqueous sodium hydroxide, and extracted with chloroform. The extract was shaken with dilute sulphuric acid and the aqueous acidic solution alkalized with aqueous sodium hydroxide and extracted with chloroform. Evaporation of the chloroform left a pale yellow foam (686 mgm.) which crystallized as plates from acetone, m.p. 214 – 217.5°. Recrystallization from acetone raised the melting point to 215 – 218° and this was unaltered by mixture with chlorodihydrogelsemine obtained by method (*a*). Calc. for $C_{20}H_{23}O_2N_2Cl$: C, 66.93; H, 6.46; N, 7.81. Found: C, 67.01; H, 6.08; N, 7.70%.

Dichlorodihydrogelsemine

A solution of dihydrogelsemine (719 mgm.) in chloroform (25 ml.), to which amalgamated aluminum (from 280 mgm. of granular aluminum) had been added, was chlorinated by the addition of a chloroform solution of chlorine (30 ml.). The mixture was allowed to stand for one hour in an ice bath and

then at room temperature for four hours. Dilute aqueous sodium hydroxide was added until the mixture was basic and the separated chloroform solution was extracted with dilute sulphuric acid. The free base obtained by extraction after alkalization of the acid solution with aqueous sodium hydroxide consisted of a colorless foam (491 mgm.) which separated as needles from acetone, m.p. 241–245°, after two recrystallizations from acetone, m.p. 249–250.5°. Calc. for $C_{20}H_{22}O_2N_2Cl_2$: C, 61.06; H, 5.64; N, 7.12. Found: C, 61.69; H, 5.80; N, 7.24%.

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THE ISOLATION AND OXIDATION OF ASPEN LIGNINS[1]

By J. M. Pepper and D. C. Hagerman

ABSTRACT

A study has been made of the conditions affecting the isolation of a lignin fraction by a procedure involving a moderate temperature catalytic hydrogenation of pre-extracted aspen wood meal. The effect of varying the initial hydrogen pressure, the catalyst, the time and maximum temperature of reaction, and the nature and acidity of the suspending medium were studied. The weight of the residual pulp, the effectiveness of lignin removal, the weight and methoxyl content of the resulting chloroform-soluble fraction containing the lignin, and the yields of vanillin and syringaldehyde obtained by the alkaline nitrobenzene oxidation of this same fraction were the factors serving as the bases for comparison.

Initial hydrogen pressures greater than 500 p.s.i.g. were not required, although below this value there was some loss of efficiency. Neither the use of water or dioxane alone was satisfactory as a suspending medium, but the mixed aqueous–organic medium was required to remove the released lignin. Considering the resultant slight acidity of the reaction product, it is suggested that in such an isolation two separate stages are involved: that of the water functioning to wet and permeate the wood and serve as the acidic medium and that of the organic solvent phase functioning to remove the liberated lignin after the hydrolytic cleavage.

Data are presented and interpreted to indicate the existence of a lignin–carbohydrate complex which is cleaved under the conditions of catalytic hydrogenation. Under the conditions of these experiments practical temperatures for lignin removal are in the range 170 – 180°C. for an aqueous–organic solvent medium, but some thirty degrees lower for an 85% acetic acid medium. Although it has been possible to isolate all the lignin, with good methoxyl recovery, consistently no more than approximately fifty per cent of the required aldehydes is obtainable on oxidation. The increasing value of the syringaldehyde – vanillin ratio with increasing temperature is due to a decreased vanillin yield.

Indications are that the use of copper chromium oxide may be preferred over Raney nickel as a catalyst for this isolation procedure.

The need for the isolation of a representative lignin fraction which has undergone no or only very slight chemical change remains a foremost problem for those interested in the fundamental chemical structure of this component. Many attempts have been made to prepare such a lignin (3). The isolation of the residual product from the periodate oxidative treatment of wood meal known as "periodate" lignin and the extraction of a lignified portion, "native" lignin, by means of cold ethanol have created the greatest interest. However it has been pointed out that the former product may have undergone partial oxidation, and the latter product unfortunately represents only a small portion, less than 10%, of the original lignin. By previously subjecting various wood samples to the decaying action of wood rot organisms, Nord has managed to increase markedly the percentage of native lignin thus obtainable (3). Whether any such pretreatment has any effect on the lignin structure is, of course, open to question.

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A method of lignin isolation that has led to the identification of interesting lignin degradation products is the catalytic hydrogenation of whole wood meal. By this method, solvent-extracted wood meal is suspended in an aqueous–organic solvent medium and heated at a moderate temperature of 165–175°C. in the presence of hydrogen gas and a nickel catalyst for two to four hours. The residual pulp may be removed by filtration and the lignin isolated from the filtrate. This product has been shown to be essentially aromatic and to consist partly of substituted phenyl ethane and phenyl propane derivatives (4, 12, 13). Although admittedly these earlier investigations have led to a highly degraded lignin fraction, the method has resulted in all of the lignin being obtainable in chloroform solution, from which it may be readily recovered for further chemical investigation. It was felt that a comprehensive study of the conditions of such an isolation technique might lead to a greatly modified process whereby the effective separation is achieved but with little chemical change in the isolated lignin fraction.

Part A. Preliminary Isolation Experiments

A series of preliminary experiments were made with a view to studying the effect on lignin removal of the nature of the suspending medium, the presence or absence of a catalyst, the initial pressure of hydrogen, and the time of reaction. A temperature of 160–180°C. was used throughout since in this range aromatic derivatives had been obtained and above which it was feared extensive ring hydrogenation would occur. The importance of this temperature range on the ease of lignin separation procedures has often been observed and is further supported by results reported herein. Samples of solvent-extracted aspen wood meal were suspended in the solvent medium, the catalyst added and the mixture heated in a high pressure reaction vessel in the presence of hydrogen gas at elevated temperatures for short periods of time. The reaction conditions for each run are outlined in Table I.

The cold reaction mixture was filtered, the acidity of the filtrate determined, and the residual pulp washed with the same solvent mixture before it was dried, weighed (allowance being made for the weight of catalyst), and a small sample tested for lignin removal using the Mäule reaction (17). For those cases in which water alone had been used as the medium a secondary extraction of the pulp with a hydrophilic organic solvent removed a further appreciable amount of product. The chloroform-soluble portions of the combined filtrate and pulp washings, and also of the secondary pulp extractives mentioned above, were obtained and dried to constant weight. Details of these observations on the reaction products are also found in Table I. The use of a total chloroform solubility as the criterion of lignin isolation was considered suitable, as a first approximation, as a comparative method of estimating lignin removal. Previous work had indicated that a chloroform extraction effected a reasonable separation of lignin products from water-soluble carbohydrate fractions.

Notwithstanding the difficulty in trying to assess the value of the variation of these conditions merely on the basis of the chloroform-solubility of the

TABLE I

PRELIMINARY EXPERIMENTS ON LIGNIN ISOLATION[a]

Run No.	Reaction conditions					H_2 absorption, moles/100 gm. lignin	Reaction products						
							Filtrate		Residual pulp				
	Medium[b]	Raney nickel,[c] gm.	Initial H_2 pressure, p.s.i.g.	Temp., °C.	Time at temp., hr.		Acidity[d]	$CHCl_3$-sol. fraction[e]	Recovery, %[f]	Mäule test[g]	Extraction solvent	$CHCl_3$-sol. fraction[e]	Total $CHCl_3$-sol. fractions[e]
1	Dioxane	35.2	2850	160–170	2	—	6	0	—	Pos.	—	—	0
2	Dioxane	18	2850	160–170	2	2	6	0	—	Pos.	—	—	0
3	Water	17.5	2900	160–170	2.5	4	5	41[h]	72	Pos.	Dioxane	59	100
5	Ethanol–water	18	3000	160–170	4	6	5	64	80	Pos.	—	—	64
6	Dioxane–water	18	3075	160–180	5	—	6	84	77	Pos.	—	—	} 100
6a	Dioxane–water	18	625	170–180	6	0.2	5.5	16	71	Sl. pos.	—	—	
7	Ethanol–water	18	425	165–175	3.5	0.2	5.5	68	80	Pos.	—	—	68
8	Dioxane–water	36	650	160–170	2.0	0.8	5.5	48	85	Pos.	—	—	48
9	Dioxane–water	18	500	170–180	5	1.4	5.0	100	55	Neg.	—	—	100
10	Dioxane–water	18	500	170–180	5	1.2	5.5	97	65	Sl. pos.	Dioxane	0	97
12	Water	18	600	170–180	5.5	2.2	4.5	52	64	Pos.	Ethanol	24	76
13	Dioxane–water	18	575	170–180	5	2.6	5.5	94	60	Sl. pos.	—	—	94
14[i]	Water	18	575	170–180	5	2.6	4.5	48	67	Pos.	Ethanol	14	62
15	Dioxane–water	18	550	170–180	5	2.8	5.5	120	58	Neg.	—	—	120
16	Dioxane–water	0	525	170–180	5	1.4	5.0	118	62	Neg.	—	—	118
17	Ethanol–water	0	550	170–180	5	0	4.5	128	63	Sl. pos.	—	—	128
18	Water	0	525	170–180	5	0	4.0	34	72	Pos.	Ethanol	56	90
19	Water	0	0	170–180	5	—	4.0	24	73	Pos.	Ethanol	50	74
20	Ethanol–water	0	0	170–180	5	—	5	120	64	Sl. pos.	—	—	120
21	Dioxane–water	0	600	170–180	5	1.0	5	130	53	Neg.	—	—	130
22	Dioxane–water	0	575	160–170	5	0	5	100	60	Sl. pos.	—	—	100

[a] *For each run, air-dried, extracted poplar wood meal (32.4 gm.); solvent medium (300 ml.).*
[b] *Binary mediums all on an equal volume basis.*
[c] *Wet weight including solvent prepared according to Pavlic and Adkins (11).*
[d] *Acidity determined by using Hydrion paper.*
[e] *Reported as percentage by weight of the original Klason lignin.*
[f] *Air-dried residue corrected for weight of catalyst.*
[g] *Distinct red coloration (pos.); red coloration on isolated fibers (sl. pos.); no coloration of fiber or solution (neg.). In no case did the Mäule reaction change on those pulps that were further extracted.*
[h] *On an ether-soluble basis.*
[i] *Charge was refluxed with Raney nickel (9 gm.) before balance (9 gm.) of nickel added.*

filtrate and Mäule reaction on the residual pulp, the following conclusions appear significant. The variation in the initial hydrogen pressure above 500 p.s.i.g. has little effect on the lignin removal, whilst below 500 p.s.i.g. there is some loss of efficiency. Then, too, the marked higher hydrogen absorption at the higher pressures would suggest a more highly hydrogenated product and therefore one of less value for future structural studies. In terms of ease of isolation there was no apparent advantage to be gained by using Raney nickel as a catalyst. In fact, the observed higher hydrogen absorption in those runs using the nickel catalyst would probably lead to a more highly reduced product. It is significant, though, that for those runs in which no catalyst was used the weight of the total chloroform-soluble fraction was consistently higher than that for those runs in which catalyst was used. This may be interpreted to indicate that there was, in the former case, the extraction into chloroform of a lignin-carbohydrate complex fraction, which, under the conditions of catalytic hydrogenation, has been cleaved to leave only the lignin as the primary chloroform-soluble portion.

The nature of the liquid medium had a marked effect on the completeness of lignin removal. The use of dioxane alone was unsatisfactory as illustrated by its failure to remove any lignin. Water alone was also ineffective as indicated by the small chloroform-soluble extract of the original filtrate. However, in these cases it is interesting to note that a subsequent extraction of the residual pulp with an organic solvent (dioxane or ethanol) removed considerably more material which must have been released under the conditions of the experiment. The most useful solvent medium was a dioxane–water (1:1) mixture, by the use of which at 170–180°C. for five hours at an initial hydrogen pressure of 500 p.s.i.g. the lignin was completely removed. Under such conditions solubility in the liquid phase is complete as illustrated by the failure of the mixture to remove any further product by a subsequent pulp extraction (Run 10).

Although the recorded acidity of the reaction filtrate does not represent a true pH value except maybe for those cases in which water alone was used, there is little doubt that some acidic component is released under the conditions of these experiments. Moreover the preferred use of the aqueous–organic medium would suggest that two separate effects are involved: that of the water functioning to permeate and wet the wood meal to later serve as the acidic medium promoting lignin separation, and that of the organic solvent phase functioning to remove the liberated lignin following the acid catalyzed hydrolytic reaction. The apparent importance, in lignin solubility studies, of the nature of the solvent has been emphasized by Schuerch (15).

Part B. Further Experiments on the Isolation and Oxidation of Aspen Lignins

It appeared that a promising method of lignin removal involved the treatment of wood meal under the conditions similar to those of Runs 10, 13, or 15. However, since this conclusion was based merely on the absence of residual lignin (Mäule test) and on the weight of the chloroform-soluble fraction, much further work was required to determine whether this fraction did contain all the lignin and whether this lignin had been altered appreciably by this extrac-

TABLE II

ISOLATION AND OXIDATION OF ASPEN LIGNINS[a]

Run No.	Raney nickel, gm.	Atmosphere		Filtrate acidity[b]	Residual pulp[c]		Chloroform-soluble products					
									Oxidation products			
		Nature	Init. press., p.s.i.g.		Yield	Mäule test	Yield[d]	OCH_3, %	Syringaldehyde, %	Vanillin, %	Total S+V	Ratio S/V
25	18	H_2	3100	5	67	Sl. pos.	102	20.1	12.4	2.85	15.25	4.35
26	18	H_2	550	5	64	Neg.	95	21.6	14.4	3.37	17.77	4.27
27	0	H_2	3025	4.5	60	Sl. pos.	145	16.4	10.4	3.37	13.77	3.1
(27 *Calculated on basis of lignin only*)								23.8			19.6	
28[e]	18	H_2	575	4.5	63	Pos.	53	23.5	13.0	1.71	14.71	7.57
							18[f]	21.2	12.1	2.40	14.5	5.04
29	0	H_2	575	5	58	Neg.	150	14.2	10.1	3.27	13.37	3.08
(29 *Calculated on basis of lignin only*)								21.3			20.0	
30	18	H_2	0	5	70	Pos.	81	19.7	14.2	4.2	18.4	3.4
31	0	H_2	0	5	68	Pos.	72	17.0	15.1	5.01	20.1	3.0
33	0	N_2	500	2	60	Pos.	128	14.2				
34[g]	0	N_2	500	2	71	Pos.	82	14.2	13.2	5.0	18.2	2.6
35[g,h]	18	H_2	500	4	86	Pos.	100	24.3	20.2	5.3	25.5	3.8
Aspen native lignin[i]								19.4	20.0	10.2	30.2	2.0
Aspen Klason lignin								17.2	Trace	Trace		
Aspen extractive free, oven-dried, based on Klason lignin content									32.5	11.5	44.0	2.82

[a] *For each run, air-dried, solvent-extracted poplar wood meal (32.4 gm.); dioxane–water (1:1)(300 ml.), temperature 175–180°C., time five hours.*
[b] *Acidity measured using Fisher alkaloid test paper.*
[c] *See Table I (f, g).*
[d] *Reported as percentage, by weight, of the original Klason lignin.*
[e] *Water only used as suspending medium, time 10 hr.*
[f] *Chloroform extract of the residual pulp.*
[g] *Temperature 165–175°C.*
[h] *Glacial acetic acid (25 ml.) added to the suspending medium.*
[i] *Kindly donated by Dr. F. E. Brauns.*

tion technique. Assuming that the major part at least of the original methoxyl content of the wood was associated with the lignin, then the methoxyl content of the chloroform-soluble fraction may be considered as a good indication of lignin removal. As a test of the chemical nature of this isolated lignin the product was oxidized with alkaline nitrobenzene and the yields of syringaldehyde and vanillin determined. Since such an oxidation of the original wood gave rise to high yields of these aldehydes, 32.5 and 11.5% of the Klason lignin, respectively, similarly obtained values from the oxidation of the isolated lignins would indicate in one respect at least the extent to which the lignin had been modified.

A second series of runs was therefore made in which the products were isolated as before but on which the above mentioned further analytical observations were made. The reaction conditions and the analyses of the various isolated lignins from each run are reported in Table II. All the chloroform-soluble fractions were fairly viscous oils at room temperature and, although originally amber to red in color, darkened considerably on standing.

Unfortunately none of the products so isolated gave the high yields of aldehydes that were obtainable from the wood itself, indicating that some chemical change had occurred which involved to some extent the groupings responsible for aldehyde formation on nitrobenzene oxidation. With the exception of Run 35, which may be significant in that acetic acid was added to the reaction mixture and gave a product of high methoxyl content and better yields of aldehydes, the total production of syringaldehyde and vanillin on oxidation was in the range 15 to 20% instead of the possible 44%. It has been pointed out by Leopold (10), in a study of this oxidation reaction, that such linkages, β-γ to the guaiacyl nucleus, as —C=C— or potentially unsaturated groupings such as $-\overset{\overset{O}{\|}}{C}-CH_2-$ and $-\overset{\overset{OH}{|}}{CH}-\overset{|}{CH}-$ are required in order to obtain high yields of vanillin. The destruction of some of these groupings is readily visualized under these reducing conditions.

The methoxyl content (20–24%) of the isolated chloroform-soluble fractions shows a high recovery of this fragment. If allowance be made for an approximate 15% of the methoxyl of aspen wood to be associated with the holocellulose (7), the actual Klason lignin has a methoxyl analysis of around 26.5%. This decreased methoxyl content may be due to direct ether cleavage and could be another factor in the decreased aldehyde yield.

The results of Runs 27 and 29 for which a significantly larger chloroform-soluble fraction of low methoxyl was obtained lend support to the belief that in those cases for which no catalyst was used some uncleaved lignin–carbohydrate complex has been removed from the wood. The methoxyl contents of the product of these two runs, if calculated as a percentage of the lignin only, assuming all the lignin to be present, are increased to 23.8 and 21.3%, respectively, and are then in agreement with those of the other runs. As an indication, too, that these fractions may represent a less changed product there are the higher total yields of aldehydes obtainable and the better syring-

TABLE III

LIGNIN ISOLATION BY HYDROGENATION

Run No.	Temp., °C. ±2.5°	Hydrogen absorption, moles per 100 gm. lignin	Residual pulp[b]		Chloroform-soluble products					
							Oxidation products			
			Yield	Mäule test	Yield[c]	OCH_3, %	Syringaldehyde, %	Vanillin, %	Total S+V	Ratio S/V
Using Raney nickel catalyst (18 gm.)[a]										
38	103	0.4	110	Pos.	4.2	7.6	8.9	3.5	12.4	2.6
39	132	0.2	112	Pos.	10.0	14.8	12.5	6.0	18.5	2.1
66	133	0.6	98	Pos.	5.9	22.1	16.7	6.5	23.2	2.6
59	137	0.0	91	Pos.	7.9	20.5	18.3	6.7	25.0	2.7
58	145	0.6	85	Pos.	20.6	24.0	19.2	4.8	24.0	4.0
61	150	0.6	77	Pos.	30.2	19.6	15.4	3.9	19.3	3.9
57	151	0.6	76	Pos.	10.2	22.2	19.4	5.0	24.4	3.9
65	153	—	74	Pos.	30.2	25.9	16.3	5.4	21.7	3.0
56	157	0.4	63	Pos.	30.0	24.3	17.8	4.3	22.1	4.2
63	160	—	81	Pos.	26.0	26.6	18.0	5.1	23.1	3.6
55	162	0.4	64	Pos.	45.5	25.5	18.6	4.4	23.0	4.3
64	166	0.0	77	Pos.	42.0	22.3	18.3	4.3	22.6	4.3
54	166	0.0	75	Pos.	31.4	24.4	18.8	4.6	23.4	4.1
60	173	0.8	60	Neg.	41	24.0	18.9	3.8	22.7	4.9
45	173	1.0	89	Sl. pos.	30	21.5	14.4	4.0	18.4	3.6
26	177	1.2	64	Neg.	94.6	21.6	14.4	3.4	17.8	4.3
62	197	2.0	58	Neg.	117	22.3	14.4	2.9	17.3	5.0
Using copper chromium oxide catalyst (12 gm.)[a]										
42	103	1.9	94	Pos.	0.8	13.7	15.5	7.4	22.9	2.1
41	133	1.2	87	Pos.	7.2	15.0	15.2	7.2	22.4	2.1
40	166	1.7	74	Pos.	38.0	14.3	16.9	5.9	22.8	2.8
52	166	1.5	50	Neg.	88	16.0	10.1	3.6	13.7	2.8
37	167	1.9	70	Sl. pos.	70	16.7	18.5	5.4	23.9	3.4
44	174	2.2	62	Neg.	—	15.0	15.4	5.5	20.9	2.8
46	175	2.8	58	Neg.	134	13.9	7.8	2.6	10.4	2.9

TABLE III (*Concluded*)

Run No.	Temp., °C. ±2.5°	Hydrogen absorption moles per 100 gm. lignin	Residual pulp[b]		Chloroform-soluble products					
			Yield	Mäule test	Yield[c]	OCH_3, %	Oxidation products			
							Syringaldehyde, %	Vanillin, %	Total S+V	Ratio S/V
36	176	1.7	72	Neg.	101	16.6	16.3	5.0	21.3	3.3
51	177	1.9	55	Neg.	128	15.8	8.2	2.8	11.0	2.9
43	187	2.9	50	Neg.	118	13.6	10.5	3.8	14.3	2.8
50	198	2.3	37	Neg.	188	11.9	4.6	1.9	6.5	2.4
48[d]	177	2.3	—	Neg.	168	14.3	5.18	2.3	7.5	2.2
49[d,e]	177	—	51	Neg.	171	13.8	5.65	2.1	7.7	2.7
Using zinc chromium oxide catalyst (12 gm.)[a]										
47	177	0.6	70	Pos.	80.5	17.2	16.9	4.7	21.6	3.6
Using acetic acid (85%) medium, Raney nickel catalyst (18 gm.)[f]										
70	106	0.8	106	Pos.	36.4	20.5	13.8	6.0	19.8	2.3
71	120	0.6	97	Pos.	58.5	19.2	15.7	4.6	20.3	3.4
69	130	0.8	100	Pos.	56.5	20.2	19.4	6.3	25.7	3.1
68	140	1.0	76	Neg.	147	16.5	10.5	3.6	14.1	2.9
67	150	2.4	90	Neg.	163	15.8	6.4	1.2	7.6	5.4

[a] *For each run, air-dried, solvent-extracted, aspen wood meal (32.4 gm.) (lignin, 5 gm.), dioxane–water (1:1) (300 ml.), Raney nickel catalyst (18 gm.) or copper chromium oxide catalyst (12 gm.); initial hydrogen pressure (cold) 500 p.s.i.g. and time, five hours at stated temperature.*

[b] *See Table I (f, g).*

[c] *Reported as percentage by weight of the Klason lignin.*

[d] *Glacial acetic acid (10 ml.) added.*

[e] *Time, 9.5 hr.*

[f] *For each run, air-dried, solvent-extracted, aspen wood meal (19.5 gm.), glacial acetic acid (155 ml.), water (27 ml.), Raney nickel catalyst (10.8 gm.); initial hydrogen pressure (cold) 500 p.s.i.g. and time, five hours at stated temperatures in a Pyrex glass liner (capacity 660 ml.) were placed inside the steel bomb which was described previously.*

aldehyde to vanillin ratio if the ratio is compared to that of the whole wood oxidations. For the other runs, the much higher ratio appears as a result of a decreased vanillin production, suggesting that the linkages associated with the guaiacyl nuclei are more readily destroyed.

Runs 33 and 34 were designed to determine whether a good isolation, albeit a lignin–carbohydrate complex, could be achieved in a nonreducing (nitrogen) atmosphere. However, delignification was not complete nor were the analyses of the isolated products of any added interest. The high acidity of the filtrate cannot be explained. The oxidations of samples of aspen "native" lignin and of aspen Klason lignin were included to indicate that by this criterion of aldehyde formation both these types of isolated lignins are not representative of the lignin in the wood.

Part C. Effect of Temperature and Catalyst on the Isolation and Oxidation of Aspen Lignins

From the foregoing experiments it appeared that a successful isolation of an only moderately changed lignin might still be possible as long as the conditions could be modified so that undue destruction of certain linkages was prevented. The effect of varying the reaction temperature and changing the type of catalyst now seemed to be the two most important studies. Lower temperature would decrease the possibility of reduction although it was realized that there was a minimum temperature for effective lignin removal. Copper chromium oxide catalyst was studied because of its known decreased tendency to reduce unsaturated linkages (1). The chemical nature of the isolated chloroform-soluble products was investigated as before. The experimental conditions for these series of runs along with the analyses of the resultant products are given in Table III.

Using the dioxane–water medium and Raney nickel catalyst, the isolated products were oils which varied in color from dark yellow to dark brown as the temperature was increased. The chloroform solutions always darkened if allowed to stand exposed to the air, but no discoloration of the solute occurred if the chloroform were removed even after prolonged exposure. In nearly all cases some crystallization occurred on long standing. From the runs made using the copper chromium oxide and zinc chromium oxide catalysts, the products were originally dark brown in color but rapidly changed to dark red on contact with air. These viscous oils slowly solidified to flaky solids but showed no signs of crystallization. The products from those experiments using 85% acetic acid and a nickel catalyst were dark red but fairly fluid oils which darkened rapidly and which showed a tendency towards crystallization.

From a consideration of the results presented in Table III a few general observations may be made. Under the conditions of these experiments, the importance, for lignin isolation, of practical temperatures in the range 170–180°C. is indicated for the use of both the nickel and copper chromium oxide catalysts in the dioxane–water medium. However, with nickel in an 85% acetic acid mixture this temperature has been lowered by some 30°C. It may be concluded that neither the presence or nature of catalyst is important for

lignin separation, but that this effect is primarily a combined result of the temperature and the acidity of the medium. The lack of sensitivity of the method and the rather empirical nature of the chloroform-solubility do not allow at this time a more accurate critical temperature to be established.

The increasing yield of the chloroform-soluble fraction with increasing temperature is consistent and to be expected. However, the methoxyl content of this fraction appears dependent to some extent on the catalyst and nature of the medium. With Raney nickel and dioxane–water, the methoxyl value parallels the increasing chloroform-solubility until a maximum is reached around 160 ± 5°C. This value is in fair agreement with that expected for the original lignin. Then as the temperature increases the methoxyl content decreases, owing possibly to partial demethylation or to dilution of the fraction with nonlignin derivatives. Under similar conditions, but replacing the nickel by copper chromium oxide catalyst, the percentage methoxyl of the isolated fractions remains quite constant (15 ± 2%) regardless of the amount extracted. This could be the result of the isolation of a definite lignin–carbohydrate fraction with a therefore lower methoxyl content than that of a similar fraction obtained using nickel which, as it has been suggested earlier, may permit the cleavage of such fragments. With nickel in acetic acid (85%) the similarly obtained methoxyl contents are again high, which tends to support the statement above.

For the great majority of the runs reported in Table III the total yield of aldehydes, expressed as a percentage of the chloroform-soluble fraction, remained between 20 and 25%, a value representing only about half that obtainable by the direct oxidation of the wood meal. For all cases in which nickel was used there is a noticeable increase in the syringaldehyde to vanillin ratio at the expense of the vanillin content, a fact that was noted in Part B. The better ratio of the aldehydes obtained using the oxide catalyst is again indicative of a less changed product.

Two other observations were made which pointed to the apparent lesser degree of hydrogenation when copper chromium oxide was used instead of nickel. One was the extra sensitivity to air oxidation of the products portrayed by their rapid darkening on standing. The second was the isolation from the filtrate of Run 52 of a chemically reactive product, no similar product being found in any runs using nickel as a catalyst. During the concentration of this filtrate, the distillate was tested with several reagents to determine whether any products were thus being removed. Positive carbonyl, Fehling's, and iodoform tests were obtained, but a phenolic test was negative. From this distillate was obtained a dark yellow oil which rapidly changed to a green, gummy substance before any further study to identify it could be undertaken. The observed properties of this substance agreed with those of methyl glyoxal but no positive identification was made. A discussion of the possible role of methyl glyoxal in plant metabolism has been given by Hibbert (8).

In review then, it appears that the sensitivity to chemical change of at least a large portion of the lignin as it exists in the wood will make its total isolation by any variation in the technique of catalytic hydrogenation a difficult task.

However, the change may not be very extensive as evidenced by the fact that a fraction containing all the lignin may be isolated. This does give rise to approximately 50% of the required aldehydes on nitrobenzene oxidation. An interesting possibility therefore arises; the separation of such an isolated lignin into two portions, depending on whether it does or does not yield aldehydes. Further chemical studies on these two portions might lead to an understanding of the linkages that have been destroyed by this method of isolation. It is realized that some of the conclusions which have been drawn from the results of this research, e.g., the isolation of a lignin–carbohydrate complex, have not been supported completely by experiment. It is possible therefore that other interpretations of the data may be made. It is hoped that subsequent investigations will permit a clearer understanding of the reactions involved.

EXPERIMENTAL

Description of Reactants

Aspen wood.—Native Saskatchewan aspen sapwood (*Populus tremuloides*) was ground in a Wiley mill (20 mesh), extracted with ethanol–benzene (4:1) for 48 hr., then with ethanol for 36 hr., thoroughly washed with water, and air dried. Anal.: Klason lignin, 16.4; moisture, 5.8; methoxyl, 5.16%.

Catalysts.—The following catalysts were prepared according to previously reported procedures: Raney nickel (11) (the washing in a hydrogen atmosphere was deleted), copper chromium oxide (2), and zinc chromium oxide (14).

Solvents.—Dioxane was purified according to Fieser (6).

General Reaction Procedure

The previously reported (12) procedure for hydrogenation was followed. The solvent extractions were made exhaustively and solvent removal procedures were continued until constant residual weights were obtained. The reaction products were studied as outlined below.

Part A.—The cooled charge, on removal from the bomb, was filtered and the acidity of the filtrate tested with Hydrion paper. The pulp was washed by stirring with two separate 250 ml. portions of the same solvent medium. These washings and the original filtrate were combined, and reduced to incipient precipitation under reduced pressure (water pump) with sufficient heat to give a moderate rate of distillation. This solution was then extracted with chloroform (5 × 300 ml.) and the chloroform layer back-extracted with water (150 ml.). The excess chloroform was removed as before and the product dried at steam bath temperature and reduced pressure (water pump). A small sample (0.1 gm.) of the pulp after being washed was retained for a Mäule test (17) and the remainder dried for 24 hr. at 100°C. A correction for the presence of nickel was made by subtracting five eighths of the weight of the wet catalyst used. The secondary pulp extractions were carried out at the reflux temperature of the extracting solvent while the mixture was being stirred mechanically. The solvent was used in as many 250 ml. portions as was necessary for complete extraction, each portion being refluxed for three

hours. The solution was reduced to incipient precipitation or a volume of 50 ml., whichever occurred the sooner, and added to chloroform (750 ml.). This mixutre was then extracted with an equal volume of water and the product recovered in the same way as that from the chloroform extract of the filtrate.

Part B.—To the charge in the bomb sodium hydrosulphite (0.5 gm.) and chloroform (50 ml.) were added as soon as the bomb was opened. The residual pulp, after removal by filtration, was extracted in a Soxhlet extractor with chloroform (200 ml.) for 10 hr. The pulp was dried at 106°C. for 24 hr., and the weight of the recovered pulp was then calculated, a correction being made for the nickel if present. A small sample (10 mgm.) of this pulp was used for the Mäule test. The original filtrate, after the acidity was determined, was extracted with three separate (50 ml.) portions of chloroform which were together back-extracted with water (50 ml.). The combined pulp and filtrate extracts were concentrated under reduced pressure (N_2 atmosphere, 30–35°C.) and finally dried to constant weight in a vacuum desiccator. This product was then analyzed for methoxyl (9), and the values reported (Table II) represent the mean of two determinations which differed from each other by less than one per cent of the Klason lignin. The alkaline nitrobenzene oxidations were made on small samples (*ca.* 10 mgm.) of this product and analyzed for the resulting aldehyde content by the method of Stone and Blundell (16).

Part C.— After filtration of the bomb contents, the pulp was washed with water (250 ml.). The volume of combined filtrate and washings was reduced to approximately 50 ml. (35°C. at 27 mm.). To the product were added water (50 ml.) and chloroform (75 ml.). The mixture was shaken and the chloroform layer removed. The water layer was further extracted with two 75 ml. portions of chloroform and these three extracts combined. The pulp was extracted in a Soxhlet extractor with chloroform (200 ml.) until no further color was removed (five hours). After drying at 100°C. for 24 hr. the weight of the recovered pulp was calculated, correction being made for the catalysts present, and a small sample used in the Mäule test. The combined pulp and filtrate extracts were dried over anhydrous sodium sulphate for 24 hr., and reduced in volume to 25 ml. (25°C. at 27 mm.). At this point the solution was transferred to a 50 ml. Erlenmeyer flask and the remaining chloroform removed under similar conditions. This product was analyzed for methoxyl content and for aldehyde production by alkaline nitrobenzene oxidation according to the methods given in Part B. The procedure and reagents used in the methoxyl determination were periodically checked by trial determinations on vanillin and those used in the aldehyde analyses were checked by repeated determinations on the extracted wood meal. Some idea of the reproducibility of this procedure is given by the following sets of analyses made at different times. The yields of syringaldehyde and vanillin, expressed as percentage of the Klason lignin, were: 31.1, 11.3; 33.2, 11.7; 31.8, 11.8; and 33.9, 11.0%.

All the reduced pressure distillations referred to above were carried out using two small "film evaporators" constructed, with modifications, according to the assembly described by Craig *et al.* (5). The main difference involved the

use of only one rotating flask, which was connected by an adapter to a ball and socket joint. A pulley system attached to this adapter provided the necessary rotation through this ball and socket joint. The socket joint was attached at a slight inclination to the center of a vertical system carrying an efficient condenser on top and a receiver flask on the bottom. A water aspirator was attached through the top of the condenser. The advantages arising from the use of such equipment with respect to the use of low temperatures, rapid concentration, and decreased foaming, were significant.

Examination of the Distillation of Run 52

During the reduction in volume of the filtrate from Run 52 (Table III), portions of the distillate were tested with several reagents to determine whether any of the products of hydrogenation were being removed. An orange red precipitate was obtained with 2,4-dinitrophenylhydrazine and positive Fehling's and iodoform tests were also obtained. A negative test for phenols was obtained using the ferric chloride – potassium ferricyanide test mixture. To recover this carbonyl containing fraction, the distillate was extracted with ether (5×50 ml.). The resulting ether–dioxane solution was shaken with moist solid sodium bisulphite until the ether solution no longer gave a positive test with 2,4-dinitrophenylhydrazine. To the solid addition product, after filtration, were added water (50 ml.) and ether (50 ml.), and the mixture was acidified with hydrochloric acid. The aqueous layer was extracted with 5×50 ml. ether and the combined ether extracts dried and concentrated at room temperature to leave a dark yellow to orange colored oil. On standing this product changed to a green, gummy substance.

ACKNOWLEDGMENTS

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TWO SYNTHESES OF 1,5:3,6-DIANHYDRO-2,4-*O*-METHYLENE-D-GLUCITOL: STABILITY OF THE METHYLENE ACETAL BRIDGE TOWARD AQUEOUS ACID[1]

By Samuel B. Baker[2]

ABSTRACT

1,5:3,6-Dianhydro-2,4-*O*-methylene-D-glucitol has been synthesized by two wholly independent routes. The methylene acetal bridge was found to be stable in hot water and dilute aqueous acid and thus differs from the methylene bridges in 1,4:3,6-dianhydro-2,5-*O*-methylene-D-mannitol and in the D-iditol analogue of the latter compound. It is suggested that this difference may be due to the ease of folding of the glucitol derivative as compared to the rigidity of the mannitol and iditol structures.

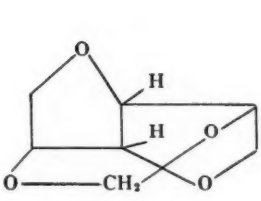
A previous (1) publication has indicated that extreme molecular rigidity occurs in cyclic compounds such as 1,4:3,6-dianhydro-2,5-*O*-methylene-D-mannitol (I) and 1,4:3,6-dianhydro-2,5-*O*-methylene-D-iditol (II) so that the strain within the bonds of I and II cannot be dissipated by folding or twisting of these bonds. It follows that these substances should be unstable and cleavage of the most highly strained group within the molecules I and II would occur. It was shown (1) that the methylene acetal groups in I and II were extremely unstable and hydrolytic cleavage occurred with great facility.

It was suggested (1) that the substance 2,5-*O*-methylene-D-mannitol (III), being capable of folding and twisting to overcome internal strain, should be stable to the hydrolytic conditions used for I and II. This was found to be the case.

Further work was undertaken to investigate the feasibility of the hypothesis and a dianhydro-*O*-methylene hexitol was synthesized that would not possess great molecular rigidity. This substance, 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol (IV), was found to be very stable toward hot water and 0.01 *N* hydrochloric acid. This stability was expected on the basis of the views postulated previously (1), as examination of a model of IV shows that the tricyclic structure may fold or twist to overcome internal strain within the molecule and the methylene acetal group should then be stable.

Vargha (2) showed that 2,4-*O*-benzylidene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (V), on treatment with one molecular equivalent of sodium methoxide, lost one *p*-tolylsulphonyl group with the formation of the ethylene oxide derivative, 5,6-anhydro-2,4-*O*-benzylidene-1-*O*-*p*-tolylsulphonyl-D-glucitol(VI). Application of Vargha's method to 2,4-*O*-methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (VII) yielded 5,6-anhydro-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (VIII). The ethylene oxide ring was very easily cleaved by dilute hydrochloric and sulphuric acids to yield 6-chloro-6-deoxy-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (IX) and 2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl -D-glucitol (X) respectively. The 6-chloro derivative (IX) on treatment with

[1]*Manuscript received January 19, 1954.*
Contribution from The Research Institute, Montreal General Hospital, Montreal, Quebec.
[2]*In charge, Division of Organic Chemistry.*



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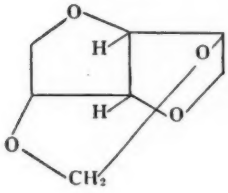

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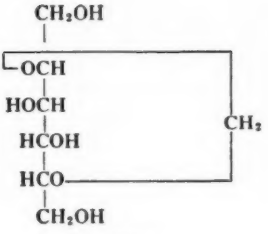

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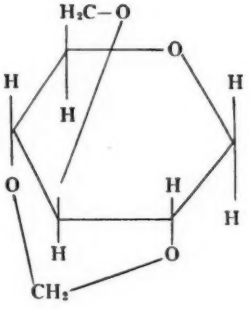

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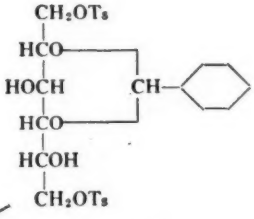

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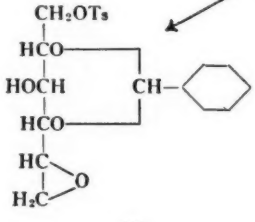

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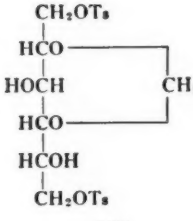

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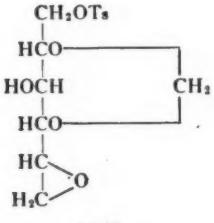

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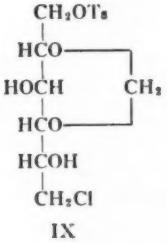

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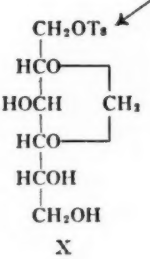

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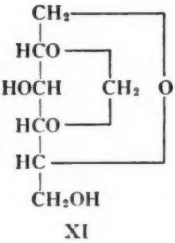

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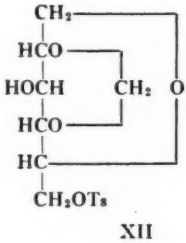
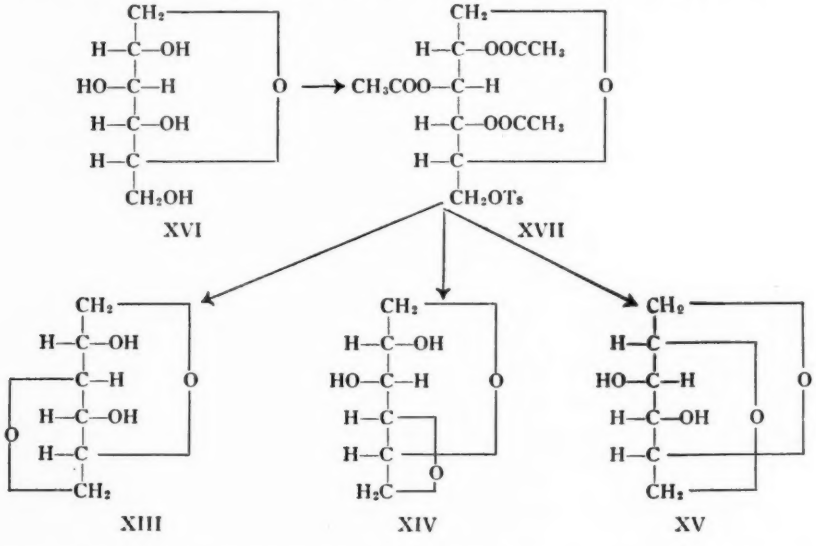


XII

one molecular equivalent of sodium methoxide yielded VIII. This showed that the chlorine atom was situated either on the terminal carbon atom or on C-5, but most probably on the terminal position since otherwise an L-iditol derivative would be obtained. Additional proof of the absence of an hydroxyl group on C-6 was obtained when tritylation of the chloro derivative IX did not occur.

The substance (X) reduced a glacial acetic acid solution of lead tetraacetate to the extent of one mole per mole oxidant thus showing the presence of vicinal hydroxyl groups in X. Monotosylation of X with tosyl chloride in pyridine yielded 2,4-*O*-methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (VII). Therefore X was a glucitol derivative, which was expected since cleavage of an anhydro ring which is on a terminal carbon atom occurs without Walden inversion. Saponification of X with aqueous sodium hydroxide yielded an anhydro derivative (XI) that reacted readily with trityl chloride in pyridine. Lead tetraacetate was not reduced, thereby indicating the absence of vicinal hydroxyl groups. Thus the anhydro ring could not be either 1,6 or 1,3. The latter ring would be unlikely on steric grounds. Therefore the substance had to be 1,5-anhydro-2,4-*O*-methylene-D-glucitol (XI). Treatment of XI with tosyl chloride in pyridine yielded the monotosylate XII, 1,5-anhydro-2,4-*O*-



methylene-6-*O*-*p*-tolylsulphonyl-D-glucitol, which on saponification with sodium methoxide yielded 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol or 2,4-*O*-methylene-*neo*glucide* (IV). This latter substance on treatment with hot water or 0.01 *N* hydrochloric acid was recovered unchanged. Hydrolysis of

**The prefix "neo" is used here to indicate analogous ring structure with neo-mannide, which is 1,5:3,6-dianhydro-D-mannitol.*

the methylene group occurred only on prolonged heating in 1 *N* hydrochloric acid. The tricyclic ring structure of IV is therefore relatively stable.

Synthesis of 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol (IV) by a different route served to confirm its structure. The D-glucitol derivative D-*neo*-glucide* (XIII) was synthesized by a route that made possible one of three structures (XIII, XIV, XV). 1,5-Anhydro-D-glucitol (polygalitol) (XVI), whose structure is known with certainty, was condensed with one molecular equivalent of tosyl chloride in pyridine and then acetylated with acetic anhydride. Isolation of the reaction product yielded a crystalline derivative that had three acetyl groups. Saponification of the latter, 2,3,4-tri-*O*-acetyl-1,5-anhydro-6-*O*-*p*-tolylsulphonyl-D-glucitol (XVII), with sodium methoxide yielded a product that could be XIII, XIV, or XV. The compounds XIV and XV having 1,2-glycol groups should be oxidized by lead tetraacetate. However, since this substance was stable to the action of this oxidant, it is very probably XIII. The product of the reactions described above,1,5:3,6-dianhydro-D-glucitol (XIII), was treated with formaldehyde solution and hydrochloric acid and the isolated product proved to be identical with 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol (IV), prepared earlier.

EXPERIMENTAL

5,6-Anhydro-2,4-O-methylene-1-O-p-tolylsulphonyl-D-*glucitol* (*VIII*)

2,4-*O*-Methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol (VII) (47.4 gm.) was dissolved in chloroform (500 cc.). Methanol (75 cc.) in which sodium (2.2 gm.) had been dissolved was added to the cold (0°) chloroform solution. A gel formed immediately and the mixture was allowed to stand overnight at 5°. The small excess of sodium methoxide was converted to carbonate, and water (100 cc.) was added to dissolve the sodium salts. The chloroform layer was separated, dried over anhydrous sodium sulphate, and concentrated *in vacuo* to a thick sirup which was then dissolved in a small volume of 99% ethanol. The solution was kept at −15° overnight and the crystalline mass, thus obtained, was washed with a little cold 99% ethanol and finally dried. The yield was 24 gm. (80%) and melting point was 94–95.5°. This substance was pure enough for subsequent work.

A sample was dissolved in a hot mixture of ethyl acetate–isopropyl ether (1:3) and, after cooling slowly to 20°, crystallization occurred in the form of clusters of rosettes. The melting point was 95–95.5°; $(\alpha)_D^{24°}$ −4.4° ($CHCl_3$; *c*, 5.6724). Anal.: Calc. for $C_{14}H_{18}SO_7$: C, 50.91; H, 5.45; S, 9.69. Found: C, 50.80; H, 5.86; S, 9.6.

Effect of Hydrochloric Acid on 5,6-Anhydro-2,4-O-methylene-1-O-p-tolylsulphonyl-D-*glucitol* (*VIII*)

The compound above (5 gm.) was heated to boiling for about one minute with 8% hydrochloric acid (120 cc.). The starting material melted, dissolved, and precipitation occurred. The precipitate was filtered, washed with water to remove all traces of acidity, and then air-dried. The yield was 4.1 gm. (74.5%). The crude product was recrystallized from ethyl acetate and the

melting point was 162–162.5° and rotation $(\alpha)_D^{25°}$ –21.2° (pyridine; *c*, 2.9048). Anal.: Calc. for $C_{14}H_{19}SClO_7$: C, 45.75; H, 5.17; S, 8.7. Found: C, 45.68; H, 5.22; S, 8.7.

A sample (1 gm.) of the above, 6-chloro-6-deoxy-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (IX), was suspended in chloroform (100 cc.) and 0.3 *M* sodium methoxide in methanol (10 cc.) was added. The solid dissolved and precipitation of sodium chloride occurred. The reaction mixture was allowed to stand overnight at 5°, the small excess sodium methoxide converted to carbonate, and the mixture washed once with a small volume of water to remove sodium salts. The chloroform solution was dried over anhydrous sodium sulphate, the solvent removed *in vacuo*, and the resulting sirup dissolved in a little 95% ethanol and the solution cooled to −15°. Precipitation occurred and water was added so that most of the product separated as a crystalline mass. The air-dried substance melted broadly at 82–92° and was recrystallized from 250 cc. of boiling isopropyl ether in a yield of 0.7 gm. (77%). Alone or in admixture with 5,6-anhydro-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol it melted at 95–96°.

*Nonreaction of Trityl Chloride with 6-Chloro-6-deoxy-2,4-O-methylene-1-O-p-tolylsulphonyl-*D*-glucitol (IX)*

A sample (0.3 gm.) of the above substance was dissolved in anhydrous pyridine (5 cc.) and trityl chloride (0.23 gm., 1 mol. equiv.) was added. The mixture was allowed to stand for three days at 24° and was then added to cold water. The crystalline substance that separated was removed by filtration and washed well with water to remove most of the pyridine. After drying in air, the solid was extracted for one hour in boiling isopropyl ether (50 cc.) and filtered. The insoluble fraction (0.24 gm.) melted at 160–162° when mixed with the starting material. The isopropyl ether filtrate was concentrated to dryness and the solid was found to be slightly impure tritanol by a mixed melting point determination with authentic tritanol. This experiment proved that the terminal carbon atom did not have an hydroxyl group and the starting material was thus 6-chloro-6-deoxy-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (IX).

*2,4-O-Methylene-1-O-p-tolylsulphonyl-*D*-glucitol (X)*

5,6-Anhydro-2,4-*O*-methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (52 gm.) was added to boiling water (1500 cc.). Concentrated sulphuric acid (15 cc.) dissolved in water (60 cc.) was added and the molten glucitol derivative (X), dissolved in about 10 min. The clear solution was quickly neutralized with barium carbonate and the barium sulphate and carbonate were removed by filtration through a thin layer of decolorizing charcoal. The clear filtrate was then concentrated *in vacuo* to a thick sirup and the latter was dissolved in hot 95% ethanol and a slight turbidity removed by filtration through a layer of charcoal. The alcoholic filtrate was then concentrated to dryness and traces of water were removed by codistillation with 99% ethanol. The colorless sirup was dissolved in 99% ethanol, petroleum ether (30–60°) was added to turbidity, and the solution cooled at −15°. Soft, feathery crystals melting at 113–

114.5° separated. The crude product was recrystallized from the same solvent mixture with practically no loss and then melted at 115–115.5°. It was soluble in acetone, ethanol, methanol, chloroform, and hot water. It was insoluble in ether and petroleum ether. It rotated $(\alpha)_D^{24°}$ –0.24° (acetone; *c*, 2.2876). Anal.: Calc. for $C_{14}H_{20}SO_8$: C, 48.27; H, 5.75; S, 9.2. Found: C, 48.15; H, 5.91; S, 9.1.

*Conversion of 2,4-O-Methylene-1-O-p-tolylsulphonyl-*D*-glucitol (VIII) into 2,4-O-Methylene-1,6-di-O-p-tolylsulphonyl-*D*-glucitol (VII)*

2,4-*O*-Methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (1 gm.) was dissolved in anhydrous pyridine (10 cc.). The solution was cooled to −5° and tosyl chloride (0.55 gm.) was added. The solution was allowed to stand for three hours after warming up to room temperature (24°) and it was then added to cold water. The crystalline product that separated was removed by filtration, washed with water on the filter, dried, and then recrystallized from 95% ethanol. It melted at 129–130° and the mixed melting point with authentic 2,4-*O*-methylene-1,6-di-*O*-*p*-tolylsulphonyl-D-glucitol was 128–130°.

*Lead Tetraacetate Oxidation of 2,4-O-Methylene-1-O-p-tolylsulphonyl-*D*-glucitol*

A sample of the compound above (0.2727 gm.)was dissolved in 0.0329 *M* lead tetraacetate in glacial acetic acid in a 100.0 ml. volumetric flask and made up to volume with the tetraacetate solution. After 1, 2, and 24 hr. 0.94, 0.99, and 1.06 mol. equiv. of lead tetraacetate were consumed.

*1,5-Anhydro-2,4-O-methylene-*D*-glucitol (2,4-O-Methylene-polygalitol)*

2,4-*O*-Methylene-1-*O*-*p*-tolylsulphonyl-D-glucitol (10 gm.) was dissolved in freshly boiled water (200 cc.). Sodium hydroxide (1.1 gm.) was added and the solution heated on the steam bath in the absence of carbon dioxide. A few drops of 1% phenolphthalein was added and after two hours the reaction mixture became neutral. The solution was then concentrated *in vacuo* and traces of water were removed by codistillation with 99% ethanol. The white crystalline residue was heated with chloroform (400 cc.) and filtered to remove the insoluble sodium *p*-toluenesulphonate. The chloroform filtrate was concentrated to about 200 cc. and petroleum ether (30–60°) was added until a faint turbidity was formed. Crystallization occurred almost immediately and the mixture was cooled to −15° overnight to assure complete crystallization. The product was found to be pure, as an additional recrystallization did not change the melting point of 135–135.5°. It rotated $(\alpha)_D^{19°}$ –24.2° (H_2O; *c*, 2.0632). Anal.: Calc. for $C_7H_{12}O_5$: C, 47.72; H, 6.82. Found: C, 47.50; H, 6.93.

*1,5-Anhydro-2,4-O-methylene-6-O-trityl-*D*-glucitol*

1,5-Anhydro-2,4-*O*-methylene-D-glucitol (3 gm.) and trityl chloride (4.7 gm.) were dissolved in anhydrous pyridine (30 cc.). The reaction mixture was allowed to stand three days at room temperature (24°). About 5 cc. water were added to dissolve the separated pyridinium chloride and the mixture was then added to cold water. The sirup that separated was dissolved in chloroform and the chloroform solution washed several times with water. The

chloroform solution was dried over anhydrous sodium sulphate, filtered and concentrated *in vacuo* to remove the solvent and traces of pyridine. The light-yellow sirup was dissolved in 99% ethanol (100 cc.) and the solution was treated with decolorizing charcoal and finally filtered. The colorless residue formed a glass that would not crystallize from any of the solvents used. Yield was 4.8 gm. (68%) and decomposition of 1.13 gm. of the substance with concentrated sulphuric acid yielded 0.68 gm. tritanol, showing the presence of one terminal hydroxyl group as the theoretical yield is 0.70 gm.

*1,5-Anhydro-2,4-O-methylene-6-O-p-tolylsulphonyl-*D*-glucitol* (*XII*)

1,5-Anhydro-2,4-*O*-methylene-D-glucitol (20 gm.) was dissolved in anhydrous pyridine (200 gm.) and the solution was cooled to 0°. *p*-Toluenesulphonyl chloride (21.0 gm.) was added and the mixture was allowed to stand four hours at 24°. The mixture was concentrated to $\frac{1}{4}$ vol. and the sirupy residue mixed with cold water (500 cc.). The sirup did not solidify; it was dissolved in chloroform and the chloroform solution washed twice with ice-cold 2% sulphuric acid to remove pyridine and once with water. The chloroform solution was dried over anhydrous sodium sulphate, filtered, and concentrated to dryness. A white crystalline substance separated in a yield of 31 gm. (81%). This was dissolved in hot 95% ethanol (200 cc.) and a trace of color removed by means of decolorizing charcoal. The clear solution was allowed to cool and crystallization occurred. The product melted at 118–119°. Further recrystallization from ethanol did not change the melting point. It rotated $(\alpha)_D^{23°}$ −16.6° ($CHCl_3$; *c*, 6.0092). Anal.: Calc. for $C_{14}H_{18}SO_7$: C, 50.91; H, 5.45; S, 9.69. Found: C, 50.83; H, 5.66; S, 9.7.

*1,5:3,6-Dianhydro-2,4-O-methylene-*D*-glucitol* (*IV*)

1,5-Anhydro-2,4-*O*-methylene-6-*O*-*p*-tolylsulphonyl-D-glucitol (15 gm.) was dissolved in chloroform (250 cc.) and sodium (2 gm.) in methanol (100 cc.) was added. The mixture became milky and after about 10 min. glistening crystals of sodium *p*-toluenesulphonate separated. The slight excess of sodium methoxide was converted to carbonate with carbon dioxide and the mixture was then concentrated to dryness *in vacuo*. The dry solid mass was broken up and extracted twice with boiling chloroform and the mixture filtered. The clear, colorless filtrate was concentrated to dryness and the solid residue was soluble in hot ether and hot ethyl acetate. Recrystallized once from ethyl acetate and twice from ether it melted at 79.5–80° and rotated $(\alpha)_D^{22°}$ −44.9° ($CHCl_3$; *c*, 1.112). The yield after recrystallization was 5.7 gm. (79%). Anal.: Calc. for $C_7H_{10}O_4$: C, 53.16; H, 6.33. Found: C, 53.07; H, 6.47.

*2,3,4-Tri-O-acetyl-1,5-anhydro-6-O-p-tolylsulphonyl-*D*-glucitol* (*XVIII*)

2,3,4-6-Tetra-*O*-acetyl-1,5-anhydro-D-glucitol (24.5 gm.) was dissolved in chloroform (300 cc.). Methanolic sodium methoxide (25 cc. of 0.2 *N*) was added and the mixture allowed to stand 36 hr. at 5°. The sodium methoxide was converted to carbonate and the solvents removed *in vacuo*. The thick sirupy product containing sodium carbonate and bicarbonate was dissolved in hot anhydrous pyridine (45 cc.) and after the solution was cooled to 0°,

tosyl chloride (13.0 gm.) was added. The reaction mixture was then allowed to stand for two hours at 22° and again cooled to 0°. Acetic anhydride (30 cc.) was added and the reaction mixture allowed to stand overnight at room temperature. The mixture was added to cold water and a sirup separated. The sirup did not crystallize after two days and it was therefore extracted with chloroform. The chloroform solution was washed with cold 5% hydrochloric acid to remove pyridine, washed twice with water, and finally dried over anhydrous sodium sulphate. The mixture was filtered and the chloroform filtrate concentrated *in vacuo*. The resulting sirup was dissolved in ether and the ether solution on cooling and scratching deposited crystals. Petroleum ether (30–60°) was added to force complete crystallization. The crude product was then recrystallized from 95% ethanol and it melted at 143.5–144.5°. It rotated $(\alpha)_D^{24°}$ 62.2° ($CHCl_3$; 1,2; *c*, 1.3816). The yield was 19.9 gm. (61%). Anal.: Calc. for $C_{19}H_{24}SO_{10}$: C, 51.35; H, 5.45; S, 7.27; Acetyl, 26.8. Found: C, 51.1; H, 5.7; S, 7.3; Acetyl, 26.5.

*Conversion of 2,3,4-Tri-O-acetyl-1,5-anhydro-6-O-p-tolylsulphonyl-*D*-glucitol to 1,5:3,6-Dianhydro-*D*-glucitol* (D-*Neoglucide*) (*XIII*)

2,3,4-Tri-*O*-acetyl-1,5-anhydro-6-*O*-*p*-tolylsulphonyl-D-glucitol (11.4 gm.) was dissolved in anhydrous methanol (150 cc.) containing sodium (0.5 gm.) in solution. The reaction mixture was allowed to stand two hours at 24° and then heated to boiling under reflux for an additional two hours. The solution was cooled to 10°, the slight excess of sodium methoxide neutralized with dilute sulphuric acid, and the neutral solution concentrated to dryness *in vacuo*. The resulting gummy mass was heated with chloroform (250 cc.) and filtered. The residue consisting mainly of sodium *p*-toluenesulphonate was extracted once with hot chloroform (75 cc.) and the combined filtrates were concentrated *in vacuo*. The resulting sirup, which was soluble in ethyl acetate, chloroform, methanol, ethanol, acetone, water, and dioxane, was heated with isopropyl ether (120 cc.) and the solution was slowly concentrated until it became turbid. Scratching the flask caused immediate precipitation. The solid mass was removed by filtration and it was recrystallized once more from a large volume of isopropyl ether. The melting point was 150–152° and the rotation was $(\alpha)_D^{24°}$ 4.1° (water: 1; 2; *c*, 1.6116). The yield was 4.9 gm. (67.5%). Anal.: Calc. for $C_6H_{10}O_4$: C, 49.25; H, 6.87. Found: C, 49.08; H, 6.97.

Lead Tetraacetate Oxidation of D-*Neoglucide* (*XIII*)

A sample (0.4062 gm.) of D-neoglucide was dissolved in 0.543 *M* lead tetraacetate in glacial acetic acid solution and then made up to 100.0 ml. in a volumetric flask with the same solution. The lead tetraacetate solution was not reduced after 2, 24, and 48 hr. This indicated the absence of a 1,2-glycol group.

Methyleneation of D-*Neoglucide*

A sample (0.3 gm.) of D-neoglucide was dissolved in 37% aqueous formaldehyde (1 cc.) and concentrated hydrochloric acid (1 cc.). The reaction mixture was allowed to stand for 20 hr. at 40–45° and the hydrochloric acid removed

with silver carbonate. Water (50 cc.) was added and the mixture filtered. The filtrate was treated with hydrogen sulphide to remove dissolved silver ions and the silver sulphide removed by filtration through a thin layer of charcoal. The filtrate was concentrated to dryness *in vacuo* and the resulting colorless sirup was dissolved in ether (3 cc.) and seeded with a crystal of 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol. The mixture was cooled to −20° for 48 hr. The crystalline product was filtered and recrystallized once more from a small volume of ether. The yield was 0.11 gm. (35%) and the product, in admixture with a sample of 1,5:3,6-dianhydro-2,4-*O*-methylene-D-glucitol, prepared as described earlier, melted at 77–80°.

Effect of Sodium Periodate and Lead Tetraacetate on 1,5:3,6-Dianhydro-2,4-O-methylene-D-glucitol (IV)

Samples of the above (IV) did not reduce either standard periodate or lead tetraacetate. This showed the absence of 1,2-glycol groups.

Effect of Acetic Anhydride on 1,5:3,6-Dianhydro-2,4-O-methylene-D-glucitol (IV)

A sample (2 gm.) of (IV) was dissolved in acetic anhydride (5 cc.) and anhydrous pyridine (5 cc.) was added. The reaction mixture was allowed to stand for 72 hr. at 23° and then converted to a thick sirup *in vacuo*. The sirupy residue was dissolved in chloroform and the chloroform solution washed once with ice-cold 2% sulphuric acid, once with saturated ice-cold sodium bicarbonate, and then with water. The chloroform solution was dried over anhydrous sodium sulphate, filtered, and concentrated to dryness *in vacuo*. The white solid residue was recrystallized once from hot ether. The yield was 1.6 gm. (80%) and the mixed melting point with the starting material (IV) was 79–80°. This indicated the absence of hydroxyl groups.

Effect of Hot Water on 1,5:3,6-Dianhydro-2,4-O-methylene-D-glucitol (IV)

A sample of the above (0.4 gm.) was dissolved in water (50 cc.) and boiled under reflux for one hour. The water was removed *in vacuo* and the distillate did not give a dimethone test for formaldehyde. The residue on recrystalliztion from ether was found to be unchanged starting material in a yield of 0.38 gm. (96%).

Effect of 0.01 N Hydrochloric Acid on 1,5:3,6-Dianhydro-2,4-O-methylene-D-glucitol (IV)

A sample of the above (0.35 gm.) was heated under reflux in 0.01 *N* hydrochloric acid (50 cc.) for one hour. The solution was neutralized with silver carbonate and then filtered. The filtrate was treated with hydrogen sulphide to remove traces of silver ions and after filtration the filtrate was concentrated to dryness and the white residue recrystallized from ether. The yield was 0.28 gm. (82%) and the mixed melting point with starting material was 78–80°.

Effect of 1 N Hydrochloric Acid on IV

The above experiment was repeated with 0.3 gm. of IV and 1 *N* hydrochloric acid. After one hour a trace of formaldehyde was formed. The solution was

then slowly distilled in a stream of nitrogen and the volume was kept constant by addition of distilled water. After six hours all the formaldehyde was evolved and 0.47 gm. (86%) of the dimethone of formaldehyde was isolated, washed, and dried. It melted at 187–189° and the melting point was not depressed with authentic formaldehyde dimethone. The residue in the distilling flask was neutralized with silver carbonate and after filtration the traces of silver ions were removed as sulphide. The filtrate was concentrated to dryness and the cloudy sirup dissolved in chloroform; the latter solution was treated with charcoal and then filtered. The clear, colorless filtrate was concentrated *in vacuo* to a thick sirup. The sirup was extracted with a large volume of boiling isopropyl ether. The solvent was allowed to evaporate slowly and crystallization occurred. The oily crystals were filtered and recrystallized once more from isopropyl ether. The yield was 0.13 gm. (48%) and the melting point was 150–152°. A mixed melting point determination with authentic 1,5:3,6-dianhydro-D-glucitol showed identity.

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NOTES

BENZIDINE-REARRANGEMENT DURING THE TITRATION OF AZO-COMPOUNDS WITH TITANOUS CHLORIDE

By Stig Veibel

Fainer, Myers, and Keirstead (1) recently mentioned that on attempting the estimation of some chlorinated azobenzenes with titanous sulphate according to the method of Knecht and Hibbert (2), using a procedure similar to that recommended by Siggia (4), they found that in some instances, viz. when the *p*-positions to the azo-group were unsubstituted, only two equivalents of titanous sulphate were used instead of the expected four equivalents; and when the *p*-positions were blocked nearly four equivalents (reported 3.27 equivalents) were used, benzidine rearrangement taking place when the *p*-positions are free.

The authors mention that Veibel (5) has reported similar rearrangements when azo-compounds are titrated with titanous chloride. They call attention to the strongly acid medium in which the reaction takes place, pointing out that this will favor the benzidine rearrangement. Evidently a procedure such as that recommended by Siggia will favor the benzidine rearrangement, but we should like to stress that a strongly acid medium is not necessary for obtaining this rearrangement during the titration. We have for more than 25 years used the technique recommended by Kolthoff and Robinson (3), in which the reaction of the medium is nearly neutral, the reaction mixture being strongly buffered with sodium citrate. The titration is carried out at room temperature and is finished in two to three minutes. Notwithstanding this, only two equivalents of titanous chloride are used when azobenzene is titrated. From this is clearly seen that even under reaction conditions not favoring the rearrangement of hydrazobenzene into benzidine such a rearrangement may take place during the titration.

Other azo-compounds may use more than two equivalents. We found, for example, that 3-nitro-azobenzene uses 8.5 equivalents of titanous chloride, which means six equivalents for the nitro function and 2.5 equivalents for the azo function. 4-Carboxy-azobenzene uses 2.05 equivalents of titanous chloride, and in estimating azo-compounds where both *p*-positions are blocked we found a consumption of three to nearly four equivalents of titanous chloride, in excellent agreement with the statement of Feiner, Myers, and Keirstead that 4,4′-dichloro-azobenzene uses only 3.27 equivalents of titanous sulphate.

When azo-compounds in which one or both *p*-positions are blocked use less than four equivalents of Ti^{+++} it means that not only a benzidine rearrangement, but a semidine or a diphenyline rearrangement as well, may take place under the conditions of the experiment, i.e. in nearly neutral solution.

The rate with which the titration is carried through may influence the number of equivalents of Ti^{+++} used. When a solution of *o*-azo-toluene is titrated in the usual manner slightly over two equivalents of titanous chloride are used, but when an excess of the titanous chloride solution is added in one batch or when, with even greater efficiency, the solution of the azo-compound is added to an excess of titanous chloride, up to three equivalents of titanous chloride are used. This result indicates that two reactions, viz. reduction to an aniline and rearrangement to a benzidine, proceed simultaneously when the initial reduction of the azo-compound to a hydrazo-compound has taken place. In the estimation of nitro-compounds we have so far never met this complication.

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THE PREPARATION OF 2,2,2-TRIFLUOROETHYLAMINE[1]

BY A. F. McKAY AND G. R. VAVASOUR

2,2,2-Trifluoroethylamine hydrochloride has been prepared (1) by the catalytic hydrogenation of 2,2,2-trifluoroacetonitrile which was obtained from 2,2,2-trifluoroacetamide on treatment with phosphorus pentoxide. The highest over-all yield by this method was 59% based on the acetamide. 2,2,2-Trifluoroethylamine hydrochloride can be produced consistently in 68–75% yields, in one step, by the reduction of trifluoroacetamide with lithium aluminum hydride.

EXPERIMENTAL

2,2,2-Trifluoroethylamine Hydrochloride

Trifluoroacetamide (50 gm., 0.44 mole) (prepared by the method of Gilman and Jones (1)) was dissolved in 200 cc. of anhydrous ether and added slowly, with stirring, to a suspension of lithium aluminum hydride (42 gm., 1.1 mole) in 600 cc. of anhydrous ether so as to maintain gentle reflux[2]. An atmosphere of nitrogen was maintained in the flask. After the addition was complete, refluxing and stirring was continued for one hour, then the theoretical amount

[1]*Issued as D.R.C.L. Report No. 141.*
[2]CAUTION: *The referee has warned that when concentrated ether solutions of lithium aluminum hydride and trifluoroacetamide are mixed, the reaction may be violent. Thus it is essential that the solutions be diluted and the additions made with extreme care.*

of water (79 cc.) was added gradually with stirring and cooling. During the addition of water the effluent hydrogen was passed through a trap cooled with dry ice – chloroform mixture. Additional water (45–60 cc.) was added slowly until the precipitate appeared white and granular. The precipitate was allowed to stand overnight and then separated by centrifugation. The solid was washed with ether, after which the washings, the contents of the trap, and the centrifugate were combined and the ethereal solution dried over Drierite. Dry gaseous hydrogen chloride was passed over the filtered ether solution and the precipated 2,2,2-trifluoroethylamine hydrochloride was recovered and dried *in vacuo* over phosphorus pentoxide, yield 44.5 gm. (75.1%). Calc. for $CF_3CH_2NH_3Cl$: Cl. 26.2%. Found: Cl, 26.35%.

2,2,2-Trifluoroethylamine

2,2,2-Trifluoroethylamine (b.p. 37.8–38.0°C. (757 mm.)) was prepared from its hydrochloride in excellent yield by the method of Gilman and Jones (1). Analysis by titration indicated that it was 99% pure.

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